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FUNDAMENTALS OF

General Chemistry

PRENTICE-HALL CHEMISTRY SERIES

WENDELL M. LATIMER, *Editor*

FUNDAMENTALS OF

General Chemistry

C. H. SORUM

Professor of Chemistry
University of Wisconsin

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Preface

There are in print today many excellent, up-to-date, general chemistry textbooks, all of them suitable for use in first-year college and university chemistry courses. In the face of such a situation the question arises as to why still another general chemistry textbook should be written. The answer is that few teachers are completely satisfied with any textbook now available and almost every teacher is looking for that ideal textbook, that ideal choice of subject matter, that ideal presentation technique that will provide the best possible tool for teaching chemistry to the average student. Because no two teachers will agree, exactly, as to what constitutes the ideal book, the ideal choice of subject matter, the ideal order of treatment, and the ideal presentation technique, and because no two students will have identical response to any sequence of written or spoken words there will never be any single completely satisfactory book. The best that any author can hope for is that he can provide a considerable number of teachers and students with a book that comes closer to their ideal than anything otherwise available. If this hope is realized the author will have made a genuine and worthwhile contribution to the teaching of chemistry. It was in pursuance of such a hope that this book was written.

C. H. Sorum

Madison, Wisconsin

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Foreword

No book, however well written, can by itself convey to a student a complete understanding and appreciation of chemistry; he must be able to see and touch and smell the things he reads about, and perform, or watch being performed, the experiments which yield the facts, laws, and generalizations which he is asked to learn and understand. To be of maximum value to a student this textbook should be supplemented, generously, by lecture demonstrations and laboratory experiments.

Reference Books

This book does not attempt to present anything but a brief picture of general chemistry. For that reason it is strongly recommended that supplementary reference books be available where they will be readily accessible to the student when he wants additional information on a subject or wants to do more advanced reading. The following books are recommended.

Textbook of Chemistry by Mack, E., Jr., Garrett, H. B., Haskins, J. F., and Verhoek, F. H. (Ginn, New York, 1949)

General Chemistry by Pauling, L. (Freeman, San Francisco, 1953)

General College Chemistry by Sneed, M. C., Maynard, J. L., and Brasted, R. C. (Van Nostrand, New York, 1954)

Principles of Chemistry and Reference Book of Inorganic Chemistry (combined volume) by Hildebrand, J. H., Latimer, W. M., and Powell, R. E. (Macmillan, New York, 1952)

Inorganic Chemistry by Moeller, T. (Wiley, New York, 1952)

How to Solve General Chemistry Problems by Sorum, C. H. (Prentice-Hall, New York, 1952)

Oxidation Potentials, 2d ed., by Latimer, W. H. (Prentice-Hall, New York, 1952)

Organic Chemistry by Hart, H., and Schuetz, R. D. (Houghton-Mifflin, New York, 1953)

CHAPTER 1

Matter, Elements, Compounds

1.1 What is chemistry? A natural question to ask, when starting the study of a new subject such as chemistry is, just what is chemistry anyway? There is no simple one-sentence answer to this question. Chemistry is concerned with so many things, so many facts, so many experiments that it cannot be defined adequately in a single sentence or paragraph. To understand fully the meaning of the word chemistry one must "live with it" for a semester or two, performing experiments, observing reactions, listening to lectures, reading books, and taking part in discussions. However, as a starting point from which to begin a study of chemistry we can say that *chemistry is a study of the properties and composition of matter and the changes that matter undergoes.*

1.2 Matter. The statement just given immediately raises such questions as: What is matter? What are properties? What are the changes that matter undergoes? *Matter is anything that has mass (weight) and occupies space.* A moment's thought will show that matter includes everything in the world that you can see or touch or smell: soil, rocks, water, trees, animals, houses, food, clothing, machinery, etc. One might be justified in feeling a bit overwhelmed at facing a subject that includes so much material. However, we will find that matter can be classified so simply that it really is not so awesome after all.

Since matter is recognized and identified by the fact that it has *mass* and occupies *space*, it is important that we become familiar with these terms and understand the units in which they are expressed.

Mass means, for all practical purposes, the same as *weight.* We are all aware of the fact that, to find the weight of an object, we simply put it on the platform or pan of a "scale" and read off the answer on the dial. Actually, though, there is a difference between weight and mass. *Weight* represents the earth's gravitational attraction for a body; it is measured by means of a simple spring balance. The weight of a body decreases as you move farther and farther away from the earth because the force of gravity decreases. The *mass* of a body represents the number of standard units of mass that are required to counterbalance the body. The

mass of an object is determined by placing it on the left pan of a balance of the type illustrated in Figure 1.1 and adding to the right pan enough weights to counterbalance it. The sum of these standard weights is the

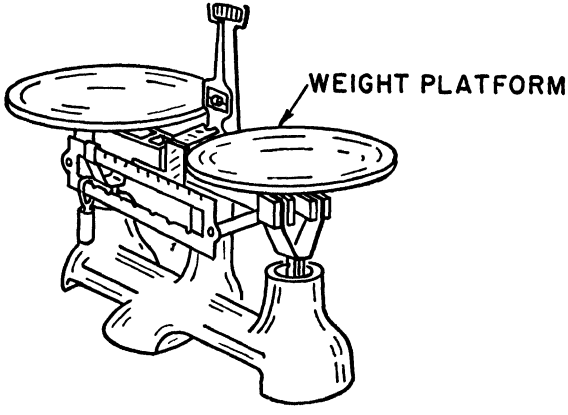


Figure 1.1. The Tripp balance. The object to be weighed is placed in a beaker or on a watch glass or piece of paper which is placed on the left pan. Standard weights are added to the right pan and the sliding weights are adjusted until the position of the pointer shows that the two pans are in balance. Weighings on this balance are accurate to 0.1 g.

mass of the object. When the two pans of the balance are exactly counterbalanced the gravitational force on each pan is the same. That means that the mass of an object is the same regardless of the altitude at which it is measured.

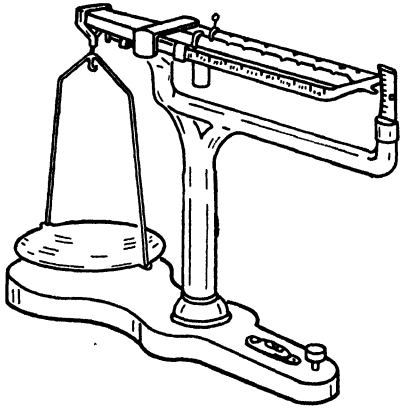


Figure 1.2. The triple beam balance. Weighings are made by adjusting the positions of the weights on the three beams. Weighings made on this balance are accurate to 0.01 g.

The spring balance has just about gone out of use. Practically all weighing, whether in the laboratory, the market, or the factory, is done with a balance type instrument (see Figures 1.2 and 1.3). That means that, strictly speaking, we are not weighing things; we are determining their mass. However, the terms weight and weighing are so widely and generally used that they have become synonymous with "mass" and "determining the mass of." In this book weight and mass will denote one and the same thing.

The *unit of mass* in the *metric*

system is the gram (g). A milligram (mg) is 1/1000 g, while a kilogram (kg) is 1000 g.

The unit of mass in the *English system* is the pound (lb). One pound is 453.59 g, and 1 kg is 2.20 lb.

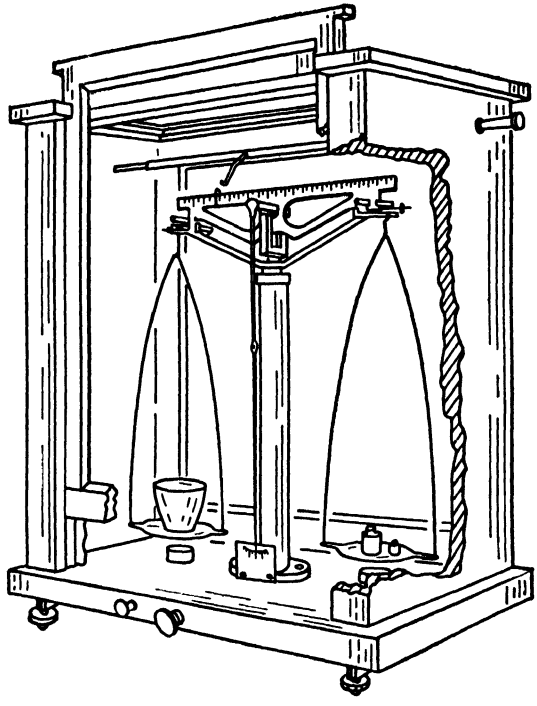


Figure 1.3. The analytical balance. Weighings can be made to an accuracy of 0.0001 g.

The unit of length in the metric system is the centimeter (cm). One hundred centimeters is 1 meter (m). One meter is 1000 millimeters (mm) or 10 decimeters (dm). One centimeter is 0.394 in., and 1 in. is 2.54 cm (see Figure 1.4).

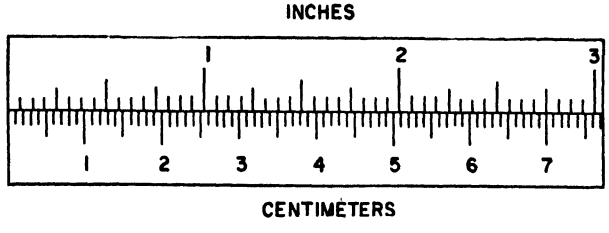


Figure 1.4. A comparison of inches and centimeters. 1 in. = 2.54 cm
1 cm = 0.394 in.

The space occupied by an object is its *volume*. The unit of volume in the metric system is the cubic centimeter (cc). The original intention was that the standard gram should be the weight of exactly 1 cc of water at a temperature of 3.98°C. One thousand cubic centimeters were then referred to as a liter (l), and 1 l of water at 3.98°C weighed 1 kg. Unfortunately, the original measurements were slightly in error; 1 g of water at 3.98°C occupies a volume of 1.000027 cc. A liter is now defined as the volume occupied by 1 kg of water at 3.98°C; a liter is therefore 1000.027 cc, not 1000 cc. A milliter (ml) is one one-thousandth of the volume of a liter. One milliliter is therefore 1.000027 cc. For all practical purposes 1 ml is the same volume as 1 cc, and 1 l is the same volume as 1000 cc; they will be so considered in this book.

The quart is a unit of volume in the English system. One quart (qt) is 946 ml, and 1 l is 1.06 qt.

Table 1.1 gives the related values of the various units of length, volume, and mass in the metric system, and the equivalent values of some of these units in the English system.

TABLE 1.1

METRIC UNITS AND EQUIVALENTS

1 centimeter (cm) = 10 millimeters (mm)	1000 ml = 1 liter (l)
10 cm = 1 decimeter (dm)	1 l = 1000.027 cc
100 cm = 1 meter (m)	1 cm = 0.394 in.
1000 mm = 1 m	1 in. = 2.54 cm
1 gram (g) = 1000 milligrams (mg)	1 m = 39.4 in.
1 kilogram (kg) = 1000 g	1 l = 1.06 quarts (qt)
1 mg = 0.001 g	1 qt = 946 ml
1 centigram (cg) = 0.01 g	1 pound (lb) = 453.59 g
1 milliliter (ml) = 1.000027 cubic centimeters (cc)	1 kg = 2.20 lb

The *mass of a unit volume* of a substance is referred to as its *density*. Since the unit of volume in the metric system is the cubic centimeter and the unit of mass is the gram, it follows that density is expressed in units of grams per cubic centimeter. One cubic centimeter of water weighs 1 g. Therefore the density of water is 1 g per cc. Density can obviously be expressed in units of grams per milliliter or, in the English system, in pounds per cubic inch or pounds per quart, etc. The concept of density is a useful one since it provides a convenient way to compare the weights of equal volumes of different materials. To say that the density of gasoline is about three-quarters as great as that of water means simply that a certain volume of gasoline weighs about three-quarters as much as an equal volume of water.

1.3 Properties. *Properties are the characteristics by which one kind of matter may be identified and distinguished from or compared with other*

kinds of matter. Copper can be distinguished from aluminum by the fact that the former is reddish orange in color, while the latter is silvery white. Color is therefore a property of matter. A rose can be identified by its characteristic fragrance. Odor can therefore be a property of matter. Coal will burn while sand will not. Therefore combustibility and noncombustibility are properties of matter. The numerous properties of matter can be placed in two categories:

A. *Physical Properties.* These are the properties, such as color, odor, density, hardness, ability to conduct heat, which matter can show without losing its identity by being destroyed. Coal is black; to display this property all the coal needs to do is allow itself to be looked at. In the process of being looked at the coal suffers no change. Likewise one can observe that water is a liquid and that glass is hard, and one can determine the density of a piece of copper and the ability of a silver wire to conduct electricity without destroying or changing each substance. These, therefore, are *physical properties.*

An iron rod can be stretched and squeezed until it becomes a long piece of iron wire. The change that the iron has undergone in being thus drawn into a wire is a *physical change* because, in the course of the change, the iron has not lost its identity as iron. The ability of iron to be drawn into a wire, referred to as *ductility*, is a physical property.

B. *Chemical Properties.* Coal will burn. To demonstrate this property the coal must actually be burned, and when it burns it is destroyed and loses its identity as coal. Such a property, the displaying of which requires that the substance undergo a change of such a nature that it loses its identity, is called a *chemical property.* The change which it undergoes is called a *chemical change*, and the process involved in this change is called a *chemical reaction.* Iron will rust; in the rusting process the iron is destroyed and loses its identity as iron. The ability to rust is therefore a chemical property of iron. In the rusting process a chemical change takes place, and a chemical reaction is involved.

Although chemistry is interested in the physical properties of matter, its chief concern we shall find is with chemical properties, chemical change, and chemical reactions. Before we proceed further with a study of these chemical aspects it will be desirable to note how the matter with which chemistry is concerned can be classified.

1.4 Classification of matter. If we were to examine all the material on earth we would easily notice that it will all fall in three classes: *solids*, such as soil, sand, gravel, stone, wood, iron, aluminum, and copper; *liquids*, such as water, gasoline, kerosene, lubricating oil, alcohol, and carbon tetrachloride; *gases*, such as air, the fuel gas that we burn, and the carbon dioxide gas that escapes from carbonated drinks. This

classification of matter is so obvious that we need say no more about it now. However, we will discuss the general properties of gases, liquids, and solids in Chapter 2.

If a trained chemist were to examine all the material on earth he would be able to separate it into two categories, *pure substances* and *mixtures* of pure substances. A typical mixture found in nature is gravel, and any one of us could easily identify it as a mixture because we would be able to see the bits of sand and other kinds of rock of which it is composed. It is distinctly heterogeneous in appearance and we would have no difficulty in picking out and separating the different constituents.

We would find other materials about us which we could easily recognize as mixtures: trees, with their bark, sapwood, heartwood, water, and complex cell structure; soil of all kinds, bread, and house paint, to mention a few. Nearly everything in nature is a mixture, but if we went into the hospitals, laboratories, chemical manufacturing plants, pharmaceutical houses, metal refineries, and drugstores we would find thousands of pure substances such as alcohol, ether, common salt, sugar, sulfur, oxygen, barium sulfate, calcium carbonate, silver nitrate, Epsom salts, iron, aluminum, silver, nickel, chromium, zinc, magnesium, lead, and baking soda. Each is identified as a pure substance because it is *homogeneous*, and its *composition* is exactly the same wherever you find it and whenever you examine it.

A trained chemist would be able to take all these pure substances and divide them into two classes, *elements* and *compounds*.

1.5 Elements. The elements are those pure substances which cannot be broken down into two or more simpler substances by the methods ordinarily available in the laboratory. A compound, in contrast, can be resolved into two or more simpler substances. *A substance is a compound if it can be resolved into two or more elements; if it cannot be broken down into two or more elements it must itself be an element.* Common salt can be decomposed into the pure substances sodium and chlorine, just by melting it and then passing an electric current through it. Neither sodium nor chlorine can be broken down into simpler substances. Therefore common salt is a compound, while sodium and chlorine are elements.

If we join the trained chemist and examine the hundreds of thousands of different substances which we might encounter, we will find that 100 of them are elements; all the rest are compounds. The complete list of these 100 elements is given on the inside of the front cover of this book. Among these elements are a number that are familiar to all of us by

name or use: aluminum, carbon, chlorine, chromium, copper, gold, iodine, iron, lead, mercury, neon, nickel, nitrogen, oxygen, plutonium, radium, silver, sodium, sulfur, tin, and uranium.

Only two elements, bromine and mercury, are liquids at ordinary room temperature. Oxygen, hydrogen, nitrogen, fluorine, chlorine, helium, neon, argon, krypton, xenon, and radon are gases. All the rest are solids.

Later on we will learn that the 100 elements may be classified in a number of ways. At this time, however, we will be interested only in the fact that a large number of the solid elements acquire a bright, shiny luster when polished. We speak of this as a *metallic luster* and we call these elements *metals*. We shall find later on that the metals have other unique properties besides this metallic luster, but for the moment we shall refer only to the latter as a means of identification. The rest of the elements, that is, the gases, one liquid, and the nonlustrous solids, we will call *nonmetals*. Some common metals, familiar to most of us, are iron, aluminum, chromium, nickel, magnesium, lead, zinc, mercury, gold, silver, and tin. Some less familiar but fairly common metals are sodium, potassium, calcium, barium, and manganese. Some common or fairly common nonmetals are carbon, sulfur, phosphorus, oxygen, chlorine, bromine, iodine, nitrogen, silicon, helium, neon, and argon.

1.6 Atoms. If we were to take a piece of one of these elements, copper for example, and divide and subdivide it we would still have copper and nothing but copper. Because it is an element we cannot break it down into two or more simpler elements. If, however, we keep on dividing and subdividing we must finally get to the smallest unit or particle of copper; that is the *atom* of copper. *The atom is the smallest unit into which an element can be divided and still retain its identity as that element.*

1.7 Atomic Weight. Suppose we were to divide and subdivide each of the 100 elements as we did copper until we had 1 atom of each. Each atom would be very small; the copper atom, for instance, is so small that 1 cc of copper (a cube of copper 1 cm on each edge) would contain about eighty-five thousand billion billion atoms. The atoms of the other elements are all of comparably small size. Small though they are, suppose, for the purpose of this discussion, that we are equipped with such powerful supermicroscopic eyes that we can actually see the atoms of these 100 elements, pick them up, and compare them with each other in weight. We would note that they all differ in weight. Suppose we line them up on the table or desk in the order of their increasing weights.

Hydrogen is the lightest and falls at the top of the line, while the unnamed element 100 is the heaviest and falls at the bottom. Helium is second on the list, just below hydrogen, oxygen is eighth, sodium is eleventh, aluminum is thirteenth, sulfur is sixteenth, chromium is twenty-fourth, copper is twenty-ninth, gold is seventy-ninth, and uranium is ninety-second.

Having arranged the atoms in the *order* of their increasing weights, we are then interested in knowing exactly how the weight of one atom *compares* with the weights of the others. What scientists have done, essentially, is to select the oxygen atom as the standard or unit of atomic mass, call its weight exactly 16, and then determine how the weight of each other atom compares with that of the oxygen atom. The values thus determined are the *atomic weights* of the elements. As a result of thousands of experiments and determinations on the part of hundreds of scientists, the atomic weights given in the table on the inside front cover of this book are recognized as the average atomic weights of the atoms. *The atomic weight of an element is therefore that number which tells how the weight of the average atom of one element compares with the weight of the average atom of every other element.* For example, the weight of the average sodium atom is to the weight of the average oxygen atom as 22.997 is to 16, the weight of the sulfur atom is to the weight of the hydrogen atom as 32 is to 1.008, and so on down the line. To say that aluminum has an atomic weight of 26.97 does not mean that the aluminum atom weighs 26.97 grams or milligrams. It means simply that it is 26.97 times as heavy as one-sixteenth of an oxygen atom.

1.8 Isotopes. In the above discussion we have spoken of "the weight of the *average atom*" of an element. The implication in this phrase is that there is more than one kind or variety of atom of a specific element. That is the situation, exactly; with a few exceptions each element has atoms with different weights. These atoms differ only in weight; their chemical properties are the same. These weight modifications are called *isotopes*. To illustrate, there are three naturally occurring isotopes of magnesium with exact atomic weights of 23.9925, 24.9938, and 25.9898; the chemical properties of the three are the same, and they are present in such proportions in ordinary magnesium that the average weight of the atoms is 24.320. This is the average atomic weight of magnesium; it represents the weight of the average atom of magnesium. The *mass number* of an isotope is that whole number which comes closest to the exact atomic weight of that isotope. The mass numbers of the isotopes of magnesium are therefore 24, 25, and 26.

Table 1.2 lists the mass numbers of the naturally occurring isotopes.

For each element its isotopes are listed in the order of their abundance, the most abundant one being placed first.

1.9 Gram-atomic weight. Gram-atom. *The gram-atomic weight is a weight in grams equal to the atomic weight.* The gram-atomic weight of helium is 4.003 g; the atomic weight of helium is 4.003. The atomic weight of sodium is 22.997; its gram-atomic weight is 22.997 g.

If one were to take exactly 4.003 g of helium and, using methods that are too involved to discuss at this point, make an actual count of the number of atoms of helium present, the answer obtained would be about 602,300,000,000,000,000,000,000 (six hundred two thousand three hundred billion billion); this number can be expressed as 6.023×10^{23}. In other words, the weight in grams of 6.023×10^{23} atoms of helium is equal, numerically, to the atomic weight of helium. The gram-atomic weight of helium is therefore the weight in grams of 6.023×10^{23} atoms of helium. If the weight of 1 atom of helium is to the weight of 1 atom of oxygen as 4.003 (the atomic weight of helium) is to 16 (the atomic weight of oxygen), then obviously the weight of 2 atoms of helium must be to the weight of 2 atoms of oxygen as 4.003 is to 16, and the weight of 6.023×10^{23} atoms of helium must be to the weight of 6.023×10^{23} atoms of oxygen as 4.003 is to 16. But we have just learned that 6.023×10^{23} atoms of helium weigh 4.003 g. Therefore 6.023×10^{23} atoms of oxygen must weigh 16 g. But 16 g is 1 gram-atomic weight of oxygen. Therefore the gram-atomic weight of oxygen, 16 g, is the weight in grams of 6.023×10^{23} atoms of oxygen. We can extend this same line of reasoning to all 100 elements and conclude that the atomic weight in grams of any element is the actual weight in grams of 6.023×10^{23} atoms of that element; the weight is called *one gram-atomic weight* or *one gram-atom.*

Why should a chemist speak of gram-atomic weights or gram-atoms of an element? Why not just talk about the weights of the individual atoms? The reason is the same as that which causes the farmer to measure wheat in bushels rather than number of individual kernels, and the housewife to measure sugar in cupfuls rather than individual grains. The kernels and grains are so small that it would be tedious and cumbersome; bushels and cupfuls are more convenient. Likewise, individual atoms are so small and light; a good-sized quantity, totaling 6.023×10^{23} atoms, is a more convenient unit to work with. Of course you can take one-half or one-fourth or one-tenth or any other fraction of a gram-atom just as you can take a fractional part of a bushel or cupful.

Knowing that the gram-atomic weight of any element is the weight in grams of 6.023×10^{23} atoms of that element, it is a relatively simple

TABLE 1.2

NATURALLY OCCURRING ISOTOPES OF THE ELEMENTS

Element	*Symbol*	*Atomic weight*	*Mass numbers of isotopes*
Actinium	Ac	227*	227, 228
Aluminum	Al	26.97	27
Antimony	Sb	121.76	121, 123
Argon	A	39.944	40, 36, 38
Arsenic	As	74.91	75
Barium	Ba	137.36	138, 137, 136, 135, 134, 130, 132
Beryllium	Be	9.02	9
Bismuth	Bi	209.00	209, 210, 211, 212, 213, 214
Boron	B	10.82	11, 10
Bromine	Br	79.916	79, 81
Cadmium	Cd	112.41	114, 112, 111, 110, 113, 116, 106, 108
Calcium	Ca	40.08	40, 44, 42, 48, 43, 46
Carbon	C	12.010	12, 13
Cerium	Ce	140.13	140, 142, 138, 136
Cesium	Cs	132.91	133
Chlorine	Cl	35.457	35, 37
Chromium	Cr	52.01	52, 53, 50, 54
Cobalt	Co	58.94	59
Copper	Cu	63.54	63, 65
Dysprosium	Dy	162.46	164, 162, 163, 161, 158, 160
Erbium	Er	167.2	166, 168, 167, 170, 164, 162
Europium	Eu	152.0	153, 151
Fluorine	F	19.00	19
Francium	Fr	223	223
Gadolinium	Gd	156.9	158, 160, 156, 157, 155, 154, 152
Gallium	Ga	69.72	69, 71
Germanium	Ge	72.60	74, 72, 70, 73, 76
Gold	Au	197.2	197
Hafnium	Hf	178.6	180, 178, 177, 179, 176, 174
Helium	He	4.003	4, 3
Holmium	Ho	164.94	165
Hydrogen	H	1.0080	1, 2
Indium	In	114.76	115, 113
Iodine	I	126.92	127
Iridium	Ir	193.1	193, 191
Iron	Fe	55.85	56, 54, 57, 58
Krypton	Kr	83.7	84, 86, 82, 83, 80, 78
Lanthanum	La	138.92	139, 138
Lead	Pb	207.21	208, 206, 207, 204, 210, 211, 212, 214
Lithium	Li	6.940	7, 6
Lutecium	Lu	174.99	175, 176
Magnesium	Mg	24.32	24, 25, 26
Manganese	Mn	54.93	55
Mercury	Hg	200.61	202, 200, 199, 201, 198, 204, 196
Molybdenum	Mo	95.95	98, 96, 95, 92, 94, 97, 100
Neodymium	Nd	144.27	142, 144, 146, 143, 145, 148, 150

TABLE 1.2 (*Cont.*)

NATURALLY OCCURRING ISOTOPES OF THE ELEMENTS

Element	*Symbol*	*Atomic weight*	*Mass numbers of isotopes*
Neon	Ne	20.183	20, 22, 21
Nickel	Ni	58.69	58, 60, 62, 64, 61
Niobium	Nb	92.91	93
Nitrogen	N	14.008	14, 15
Osmium	Os	190.2	192, 190, 189, 188, 187, 186, 184
Oxygen	O	16.000	16, 18, 17
Palladium	Pd	106.7	106, 108, 105, 110, 104, 102
Phosphorus	P	30.98	31
Platinum	Pt	195.23	195, 194, 196, 198, 192
Polonium	Po	210*	210, 211, 212, 214, 215, 216, 218
Potassium	K	39.096	39, 41, 40
Praseodymium	Pr	140.92	141
Protactinium	Pa	231	231, 234
Radium	Ra	226.05	223, 224, 226, 228
Radon	Rn	222	222, 220, 219
Rhenium	Re	186.31	187, 185
Rhodium	Rh	102.91	103
Rubidium	Rb	85.48	85, 87
Ruthenium	Ru	101.7	102, 101, 104, 100, 99, 96
Samarium	Sm	150.43	152, 154, 147, 149, 148, 150, 144
Scandium	Sc	45.10	45
Selenium	Se	78.96	80, 78, 76, 82, 77, 74
Silicon	Si	28.06	28, 29, 30
Silver	Ag	107.880	107, 109
Sodium	Na	22.997	23
Strontium	Sr	87.63	88, 86, 87, 84
Sulfur	S	32.06	32, 34, 33
Tantalum	Ta	180.88	181
Tellurium	Te	127.61	130, 128, 126, 125, 124, 122, 123, 120
Terbium	Tb	159.2	159
Thallium	Tl	204.39	205, 203, 207, 208, 210
Thorium	Th	232.12	227, 228, 230, 231, 232, 234
Thulium	Tm	169.4	169
Tin	Sn	118.70	120, 118, 116, 119, 117, 124, 122, 112, 114, 115
Titanium	Ti	47.90	48, 46, 47, 49, 50
Tungsten	W	183.92	184, 186, 182, 183, 180
Uranium	U	238.07	238, 235, 234
Vanadium	V	50.95	51
Xenon	Xe	131.3	132, 129, 131, 134, 136, 130, 128, 124, 126
Ytterbium	Yb	173.04	174, 172, 173, 171, 176, 170, 168
Yttrium	Y	88.92	89
Zinc	Zn	65.38	64, 66, 68, 67, 70
Zirconium	Zr	91.22	90, 92, 94, 91, 96

* Mass number of most plentiful isotope.

matter to calculate the actual weight in grams of one single atom of that element. For copper the calculation would be 63.54 g $\div$ 6.023 $\times$ 10^{23} atoms = 1.05 $\times$ 10^{-22} g per atom.

Suppose instead of counting out 6.023 $\times$ 10^{23} atoms of oxygen to give a weight of 16 g we were to count out enough atoms so that their weight was 16 lb; let us say that it takes Y atoms of oxygen to weigh 16 *pounds*. If Y atoms of oxygen weigh 16 lb, then Y atoms of sulfur will weigh 32 lb, Y atoms of hydrogen will weigh 1.008 lb, Y atoms of sodium will weigh 23 lb, and so on down the list of elements. That means that 23 lb of sodium is 1 *pound-atomic weight* of sodium, and 32 lb of sulfur is 1 *pound-atom* of sulfur. Similarly, we can speak of a *ton-atomic weight* and a *ton-atom*. The numerical value of the atomic weight can be expressed in any mass unit.

1.10 Symbols. It is convenient to refer to an element by use of an abbreviation, called a *symbol*, rather than the full name. The symbols of the 98 named elements are given in the table on the front cover. In most cases the symbol is the abbreviation of the name of the element as given. Thus Al is the abbreviation for aluminum. In a few instances it is an abbreviation for the Latin or Greek name. Thus antimony is Sb from *stibnium*, copper is Cu from *cuprum*, gold is Au from *aurum*, iron is Fe from *ferrum*, lead is Pb from *plumbum*, mercury is Hg from *hydrargyrum*, potassium is K from *kalium*, silver is Ag from *argentum*, sodium is Na from *natrium*, and tin is Sn from *stannum*. Tungsten was at one time called *wolframium* and the abbreviation W for the latter name is still used. When the symbol of an element is used in any sort of chemical notation it always refers to a definite quantity of that element; it represents as many parts by weight of that element as there are units in its atomic weight. Thus the symbol S, for sulfur, refers to 32.06 parts by weight of sulfur; likewise, the symbol Al refers to 26.97 parts by weight of aluminum. The symbols S and Fe in the *equation* S + Fe = FeS do not refer to some indefinite quantity of sulfur and iron; they designate that sulfur and iron are involved in the exact ratio of 32.06 parts by weight (1 atomic weight) of sulfur to 55.85 parts by weight (1 atomic weight) of iron. If the weights are being measured in grams, as is generally the case, then S refers to 32.06 *grams* of sulfur and Fe refers to 55.85 *grams* of iron; in this case *the symbol represents 1 gram-atom* (1 gram-atomic weight) of an element. If weights are measured in pounds or tons, the symbols in the above equation represent a ratio of 32.06 *pounds* of sulfur to 55.85 *pounds* of iron or 32.06 *tons* of sulfur to 55.85 *tons* of iron; in this case the symbol represents 1 pound-atom (1 pound-atomic weight) or 1 ton-atom (1 ton-atomic weight). This quantitative

significance of the symbol is, we shall find, of very great importance in the solving of chemical problems.

A specific isotope of an element is indicated by placing the mass number of the isotope as a superscript to the symbol. Thus U^{235} refers to the uranium isotope with a mass number of 235.

1.11 Compounds. We have already stated that a compound is a substance that can be broken down into two or more elements. Common salt is a compound; it can be decomposed into the elements sodium and chlorine. Water is a compound; it can be resolved into oxygen and hydrogen. Sugar is a compound; it yields carbon, oxygen, and hydrogen when broken down completely.

When sodium and chlorine are brought together they combine to form the compound common salt. Likewise hydrogen combines with oxygen to form water, magnesium combines with oxygen to form the compound magnesium oxide, and iron combines with sulfur to form the compound iron sulfide. We could extend this list to include hundreds of compounds.

Just what happens when two or more elements combine to form a compound, how can we be sure that a compound has been formed, and by what tests can we determine whether or not a substance is a chemical compound?

To help answer these questions all we need do is burn some magnesium in a jar of oxygen gas and observe exactly what happens. Here is what we would notice:

(a) As the magnesium burns, a brilliant white light is generated and a large amount of heat is given off. Since light and heat are forms of *energy* we can conclude that energy has been given off during the reaction.

(b) The magnesium and oxygen are used up and a completely new substance is formed. Whereas magnesium is a shiny metal and oxygen is a colorless gas, the new substance is a white powder.

(c) The white powder is completely homogeneous, whereas the mixture of solid magnesium and oxygen gas was heterogeneous.

(d) Particles of magnesium cannot be picked out of the white powder.

(e) Most important of all, if we repeat the experiment many times we observe that the magnesium and oxygen always combine in exactly the same ratio by weight, and this ratio we find by exact measurement is 24.32 parts by weight of magnesium to 16.00 parts by weight of oxygen. If we weigh out exactly 24.32 g of magnesium, it combines with exactly 16.00 g of oxygen to form 40.32 g of white powder which we will call magnesium oxide. If we use exactly 12.16 g of magnesium, it com-

bines with exactly 8.00 g of oxygen, and if we use 1.216 g of magnesium, it combines with exactly 0.800 g of oxygen. If 24.32 g of magnesium are burned in a flask containing 17 g of oxygen, the magnesium will combine with exactly 16 g of oxygen; the extra gram of oxygen will remain behind in the flask.

If we examine hundreds of compounds either by *synthesizing* them (forming them from the elements as we did magnesium oxide) or by *analyzing* them (breaking them down into their component elements), we get the same results that we did with the magnesium oxide. We can conclude, therefore, that the following facts are true for all chemical compounds.

1. *The composition of a given compound is always the same; it is definite and exact.* Magnesium oxide always contains magnesium and oxygen combined in the exact ratio of 24.32 parts by weight of magnesium to 16.00 parts by weight of oxygen. Carbon dioxide always contains carbon and oxygen combined in the exact ratio of 12.01 parts by weight of carbon to 32.00 parts by weight of oxygen. Common salt always contains sodium and chlorine combined in the ratio of 22.997 parts by weight of sodium to 35.46 parts by weight of chlorine, ethyl alcohol always contains carbon, oxygen, and hydrogen combined in the ratio of 24.02 parts by weight of carbon to 6.048 parts by weight of hydrogen to 16.00 parts by weight of oxygen, and so on down the entire list of chemical compounds. This exactness of composition of compounds is referred to as the *law of definite composition.*

2. *When elements combine to form compounds, energy is either liberated or absorbed.* Energy in the form of heat is usually given off when elements combine to form a compound, and the reaction is said to be *exothermic.* In some reactions, heat energy is absorbed when the compound is formed, and the resultant reaction is said to be *endothermic.* The heat energy that is given off or taken up when a compound is formed is called its *heat of formation.*

3. *Elements lose their identity, their characteristic properties, when they combine to form a compound.* The compound that is formed has characteristic new properties different from those of the elements from which it was formed. This means that the formation of a compound from its constituent elements is a chemical change and involves a chemical reaction. The ability of elements to combine to form a compound illustrates a chemical property of each element.

4. *The compound substance is homogeneous.* Separate particles of the constituent elements cannot be distinguished under the most powerful microscope; the material is the same throughout. Since the compound is homogeneous, it obviously cannot be separated into its constituent elements by a simple mechanical process.

In contrast with compounds, *mixtures are not of definite composition; they are generally not homogeneous, and the component substances retain their individual identities and are separable by simple mechanical means.* (*Solutions*, which will be discussed in detail in Chapter 11, are homogeneous mixtures.)

1.12 Formulas of compounds. Because a specific compound always contains the same elements combined in exactly the same ratio by weight, it is possible to represent its composition by means of a *formula.* To illustrate, we learned that magnesium always combines with oxygen in the ratio of 24.32 parts by weight of magnesium to 16.00 parts by weight of oxygen. That means that 24.32 g of magnesium combine with exactly 16.00 g of oxygen to form 40.32 g of magnesium oxide. The atomic weight of magnesium is 24.32, and that of oxygen is 16; 24.32 g is 1 gram-atom of magnesium, and 16.00 g is 1 gram-atom of oxygen. The symbol for magnesium is Mg, and as we have already learned, it represents 1 gram-atom of magnesium. The symbol for oxygen is O, and it represents 1 gram-atom of oxygen. Therefore the composition of the compound magnesium oxide can be represented by the formula MgO. This formula tells us that the compound is made up of magnesium and oxygen combined in the *ratio* of 1 gram-atom of magnesium to 1 gram-atom of oxygen, that is, in the ratio of 1 atom of magnesium to 1 atom of oxygen.

Carbon combines with oxygen in the ratio of 12.01 g of carbon to 32.00 g of oxygen; 12.01 g is 1 gram-atom of carbon, 32 g is 2 gram-atoms of oxygen. That means that carbon dioxide is made up of carbon and oxygen combined in the ratio of 1 gram-atom of carbon to 2 gram-atoms of oxygen. The formula is therefore CO_2; the subscript 2 refers only to the oxygen and means that there are 2 gram-atoms of oxygen.

Hydrogen combines with oxygen in the ratio of 2.016 g of hydrogen to 16 g of oxygen; that is a ratio of 2 gram-atoms of hydrogen to 1 gram-atom of oxygen. The formula for water is therefore H_2O.

As has already been stated, 12.16 g of magnesium combine with 8.00 g of oxygen to form 20.16 g of magnesium oxide. Now 12.16 g of magnesium is $\frac{1}{2}$ gram-atom, and 8.00 g of oxygen is also $\frac{1}{2}$ gram-atom. The formula of magnesium oxide would then appear to be $Mg_{0.5}O_{0.5}$. The ratio of 0.5 to 0.5 is the same as 1 to 1. So the simplest formula is MgO. In writing the formula a *simple whole-number ratio* is used.

Suppose we found by actual experiment that 2.12 g of copper combined with 0.53 g of oxygen to form 2.65 g of copper oxide. How shall we go about finding the formula of the oxide? As in the cases cited above, to find the formula we must find how many gram-atoms of copper combine with how many gram-atoms of oxygen. To find the number of

gram-atoms of an element we will, as we did above, divide the number of grams of the element by the weight in grams of 1 gram-atom of the element. Thus 2.12 g of copper ÷ 63.54 g per gram-atom = 0.033 gram-atom of copper; 0.53 g of oxygen ÷ 16 g per gram-atom = 0.033 gram-atom of oxygen. The ratio of 0.033 to 0.033 is the same as 1 to 1, so the formula is CuO.

Suppose we analyze an unknown compound and find that it contains 31.9% potassium, 28.9% chlorine, and 39.2% oxygen. How shall we calculate the formula of the compound? Per cent means "parts per 100." Therefore to say that a compound contains 31.9% potassium, 28.9% chlorine, and 39.2% oxygen is equivalent to saying that 100 g of the compound contains 31.9 g of potassium, 28.9 g of chlorine, and 39.2 g of oxygen. Here again, *to find the formula we must find the relative number of gram-atoms of each element present.* Therefore, 31.9 g of potassium ÷ 39.1 g per gram-atom = 0.815 gram-atoms of potassium; 28.9 g of chlorine ÷ 35.46 g per gram-atom = 0.815 gram-atoms of chlorine; and 39.2 g of oxygen ÷ 16 g per gram-atom = 2.45 gram-atoms of oxygen. The ratio of gram-atoms of potassium to gram-atoms of chlorine to gram-atoms of oxygen is 0.815 to 0.815 to 2.45. To reduce this to a small whole-number ratio we will divide each number by the smallest, which is 0.815. That gives a ratio of 1 gram-atom of potassium to 1 gram-atom of chlorine to 3 gram-atoms of oxygen. The formula is therefore $KClO_3$.

We can summarize the method illustrated in the above examples as follows:

1. Determine the exact composition of the compound, that is, the weights of each element that combine, or the per cent of each element in the compound, either by analysis or synthesis.

2. Divide the weight of each element, or the per cent of each element by its gram-atomic weight. The simplest ratio between the quotients gives the *simple chemical formula,* called also the *empirical formula.*

The formulas of the thousands of compounds that will be encountered in the study of chemistry have all been determined from actual experimental data in the manner just outlined. Certain additional experimental evidence may be introduced to determine whether the simple formula is in fact the true formula, but that need not concern us at this moment.

1.13 Molecules and ions. We have learned that the atom is the smallest unit into which an element can be divided and still retain the properties of the element. There is, obviously, a smallest unit in which a compound can exist and still retain the properties of the compound;

however, the nature of this unit varies from one group of compounds to another, so it cannot be so simply depicted and described as in the case of the atom. For a great many compounds the unit is a neutral particle whose composition, in terms of atoms, is represented correctly by the empirical formula of the compound. This particle is called a *molecule*. Thus the smallest particle of carbon dioxide is a *molecule* of CO_2, consisting of 1 atom of carbon in combination with 2 atoms of oxygen. The formula CO_2 is the *true chemical formula* for carbon dioxide; it represents the true composition of a molecule of the compound. Similarly, H_2O, H_2S, HCl, CO, CH_4, NH_3, H_2Se, H_2Te, SO_2, and CS_2 are true chemical formulas; the unit particle of each of these compounds is a *molecule* made up of the number and kind of atoms represented by the formula.

For a small number of compounds the unit particle is a neutral molecule, but the composition of this molecule is represented by a simple multiple of the empirical formula. Thus the smallest particle of acetylene is made up of 2 atoms of carbon in combination with 2 atoms of hydrogen. Its composition is represented correctly by the true chemical formula C_2H_2; the empirical formula would be CH. This particle also is called a molecule. The compounds benzene, ethane, butane, and cyanogen exist as molecules whose compositions are represented correctly by the true chemical formulas C_6H_6, C_2H_6, C_4H_{10}, and C_2N_2, respectively.

For a few substances the composition of the molecule will vary with the conditions under which it exists. For example, the composition of the hydrogen fluoride molecular species may be correctly represented as HF, H_2F_2, H_3F_3, or H_6F_6, depending on the conditions. Likewise, aluminum chloride exists as $AlCl_3$ and Al_2Cl_6.

A very large number of compounds do not exist as simple neutral molecules. Instead, they consist of electrically charged particles called *ions*. We will learn more about these ions later. At the present we will say only that a compound such as common salt, whose composition is represented correctly by the empirical formula NaCl, is made up of positively charged sodium ions (Na^+) and negatively charged chloride ions (Cl^-); these ions are the smallest particles in which common salt can exist and display its properties. There is then, actually, no such thing as a molecule of sodium chloride in the sense in which a molecule has been described. In any quantity of common salt, whether it is in the form of a solid, a liquid melt, or a solution, the Na^+ and Cl^- ions are always present in the ratio of 1 Na^+ ion to 1 Cl^- ion. Therefore the composition of the salt is represented correctly by the empirical formula NaCl. It is important to remember, however, that the use of the formula NaCl is not to be interpreted as meaning that common salt exists in the

form of NaCl molecules. What has been said about NaCl applies to hundreds of compounds such as KCl, $BaCl_2$, MgO, $CuSO_4$, and AgBr. Later, we will learn what determines whether a compound exists as molecules or ions, that is, whether it is molecular or ionic in nature.

In the above discussion the term molecule has been applied only to compounds. It should, however, be pointed out at this time that the term is also applied to unit particles of elements. Thus we will speak correctly of molecules of oxygen, hydrogen, and copper. In its broader sense the term molecule refers to the smallest neutral particle in which any substance exists and displays the characteristic properties of that substance.

1.14 Formula weight. Molecular weight. Mole. The sum of the atomic weights of the atoms represented by the formula of a substance is the *formula weight* of that substance. If the formula is the true chemical formula, the formula weight is also the *molecular weight* of the substance. Thus the formula weight of NaCl is 58.5; this value is obtained by adding the atomic weight of sodium (23.0) to the atomic weight of chlorine (35.5). The formula weight of CO_2 is 44.0; this value is obtained by adding the atomic weight of carbon (12.0) to 2 atomic weights of oxygen (32.0). Because CO_2 is the true chemical formula of carbon dioxide, 44.0 is the molecular weight of CO_2. Since NaCl is only the empirical formula of NaCl, 58.5 is not the true molecular weight of NaCl; it is only the formula weight. The formula weight can be calculated for any substance whose formula, either empirical or true chemical, is known; to calculate the molecular weight of a substance its true chemical formula must be known. Since the molecular weight is the sum of the atomic weights of the atoms in the molecule, and since the atomic weight is the ratio of the weight of an atom to a standard reference atom, it follows that the molecular weight of a substance gives the ratio of the weight of a molecule of that substance to the weight of the above standard reference atom. Thus, to say that the molecular weight of CO_2 is 44 means that the weight of the molecule of CO_2 is to the weight of the atom of oxygen as 44 is to 16.

The *gram-formula weight* of a substance is a weight *in grams* equal to the formula weight. Thus the formula weight of NaCl is 58.5; the gram-formula weight of NaCl is 58.5 *grams*. Likewise, the *gram-molecular weight* of a substance is the molecular weight expressed in units of grams. Thus the molecular weight of CO_2 is 44.0; the gram-molecular weight of CO_2 is 44.0 *grams*. If the unit of mass that is being used is the pound or ton rather than the gram, the formula weight and molecular weight, expressed in these units, are, respectively, the *pound-formula*

weight, *ton-formula weight*, *pound-molecular weight*, and *ton-molecular weight*. Thus the pound-formula weight of NaCl is 58.5 *pounds*, and the ton-molecular weight of CO_2 is 44.0 *tons*.

It is common practice to use the term *mole* in place of the longer terms, gram (pound, ton) formula weight and gram (pound, ton) molecular weight. The term mole refers to the sum of the weights of the atoms represented by the formula of the substance expressed in whatever unit of mass that is being used. Thus 1 *gram*-mole of NaCl is 58.5 g, 1 *pound*-mole of CO_2 is 44.0 lb, and 1 *ton*-mole of H_2SO_4 is 98.1 tons. Since the unit of mass commonly employed in chemistry is the gram, the term mole will be understood to mean *gram*-mole unless specifically stated otherwise. If only the empirical formula of a substance is known, 1 mole means 1 gram-formula weight. If the true chemical formula of a substance is known, 1 mole means 1 gram-molecular weight. In any case the term mole, when applied to any substance, refers to that weight which is represented by the formula of the substance, whether it is a true chemical formula or an empirical one.

Since the molecular weight has been defined in such a way that it can be determined only if the true chemical formula, and hence the true chemical composition, of a molecule of the substance is known, it must follow that the gram-molecular weight of a substance is the actual weight in grams of 6.023×10^{23} molecules of the substance. To illustrate the reasoning that leads to this conclusion, we have learned that 6.023×10^{23} atoms of carbon (12.01 g or 1 gram-atomic weight) combine with $2 \times 6.023 \times 10^{23}$ atoms of oxygen (32.00 g or 2 gram-atomic weights). Since 1 molecule of CO_2 consists of 1 atom of carbon and 2 atoms of oxygen, it follows that the 6.023×10^{23} atoms of carbon and $2 \times 6.023 \times 10^{23}$ atoms of oxygen must have yielded 6.023×10^{23} molecules of carbon dioxide. This carbon dioxide weighs 44.0 g, which is 1 gram-molecular weight. Therefore 1 gram-molecular weight of CO_2 is the actual weight in grams of 6.023×10^{23} molecules. In an analogous manner we can reason that *1 gram-molecular weight of any substance is the weight in grams of* 6.023×10^{23} *molecules of that substance.* It must follow, also, from our definition, that 1 gram-mole of a substance whose true molecular weight is known consists of 6.023×10^{23} molecules.

1.15 Names of chemical compounds. Having learned how the formulas of compounds are derived, it is important to get acquainted with some of these formulas and learn how they are named. Certain aspects of the basis for the naming system cannot, however, be presented until the structure of atoms and molecules has been taken up in Chapters 6 and 7.

Table 1.3 gives the chemical name and the chemical formula (either empirical or true) of each of a number of typical compounds that will be encountered in the course. In certain instances the common name is given in parentheses directly under the chemical name. A careful examination of this list reveals certain rules that are followed in naming a compound.

1. *The name of a binary compound* (one that contains only 2 elements) *always ends in "ide."* MgO, magnesium oxide; $ZnCl_2$, zinc chloride; $CaBr_2$, calcium bromide.

2. *If the compound contains a metal its symbol and name appear first.* The name of the element (nonmetal) with which the metal is combined is shortened and attached to the appropriate suffix: CaO, calcium oxide; $AlCl_3$, aluminum chloride; PbS, lead sulfide; $CuSO_4$, copper sulfate.

3. *When combinations of elements recur in compounds they are treated*

TABLE 1.3

NAMES OF CHEMICAL COMPOUNDS

Formula	*Name*	*Formula*	*Name*
MgO	magnesium oxide	KI	potassium iodide
H_2O	hydrogen oxide (water)	$CaBr_2$	calcium bromide
CaO	calcium oxide	PbS	lead sulfide
ZnO	zinc oxide	H_2SO_4	hydrogen sulfate (sulfuric acid)
HgO	mercury oxide		
Ag_2O	silver oxide	$CuSO_4$	copper sulfate
Al_2O_3	aluminum oxide	Na_2SO_4	sodium sulfate
CO_2	carbon dioxide	$MgSO_4$	magnesium sulfate
SiO_2	silicon dioxide	$Al_2(SO_4)_3$	aluminum sulfate
P_4O_{10}	phosphorus oxide	HNO_3	hydrogen nitrate (nitric acid)
HCl	hydrogen chloride		
HF	hydrogen fluoride	KNO_3	potassium nitrate
HBr	hydrogen bromide	$Zn(NO_3)_2$	zinc nitrate
HI	hydrogen iodide	H_2CO_3	hydrogen carbonate
H_2S	hydrogen sulfide	$CaCO_3$	calcium carbonate
NaCl	sodium chloride (common salt)	Na_2SO_3	sodium sulfite
		KNO_2	potassium nitrite
KCl	potassium chloride	$KClO_3$	potassium chlorate
$CuCl_2$	copper chloride	$KClO_2$	potassium chlorite
$MgCl_2$	magnesium chloride	KClO	potassium hypochlorite
$ZnCl_2$	zinc chloride	$KClO_4$	potassium perchlorate
$AlCl_3$	aluminum chloride	NaOH	sodium hydroxide
$CrCl_3$	chromium chloride	KOH	potassium hydroxide
CCl_4	carbon tetrachloride	$Ca(OH)_2$	calcium hydroxide
PCl_5	phosphorus pentachloride	$Al(OH)_3$	aluminum hydroxide
NH_3	ammonia	CH_4	methane
NaF	sodium fluoride		

as a unit and are named as a unit. These units are called *radicals* or *groups.* Examples are the sulfate radical SO_4, in H_2SO_4, $CuSO_4$, Na_2SO_4, $MgSO_4$, and $Al_2(SO_4)_3$ (the parenthesis with a subscript 3 means that the compound contains three sulfate radicals in combination with two atoms of aluminum), the nitrate radical NO_3, in HNO_3, KNO_3, $Zn(NO_3)_2$, the carbonate radical in H_2CO_3, $CaCO_3$, the sulfite radical in Na_2SO_3, the nitrite radical in KNO_2, the chlorate radical in $KClO_3$, the chlorite radical in $KClO_2$, and the hydroxide radical in NaOH, KOH, $Ca(OH)_2$, $Al(OH)_3$. The radicals encountered in this course will generally contain a nonmetal in combination with oxygen. The name of this nonmetal, with an appropriate suffix, gives the name of the radical: SO_4, sulfate; NO_3, nitrate; CO_3, carbonate; ClO_3, chlorate. Compounds made up of radicals contain more than 2 elements and are called *ternary* compounds.

4. *The name of a ternary compound ends in "ate" or "ite"* (an exception to this rule is furnished by the hydroxides): $MgSO_4$, magnesium sulfate; $Zn(NO_3)_2$, zinc nitrate; $CaCO_3$, calcium carbonate; Na_2SO_3, sodium sulfite; KNO_2, potassium nitrite; KClO, potassium hypochlorite; $KClO_4$, potassium perchlorate.

5. *The ternary compound whose name ends in "ite" always contains one less atom of oxygen per unit than the corresponding "ate" compound:* Na_2SO_4, sodium sulfate and Na_2SO_3, sodium sulfite; KNO_3, potassium nitrate, and KNO_2, potassium nitrite; $KClO_3$, potassium chlorate, and $KClO_2$, potassium chlorite.

6. *A ternary compound carrying the prefix "per" contains one more atom of oxygen than the related "ate" compound:* $KClO_4$, potassium perchlorate, and $KClO_3$, potassium chlorate.

7. *A ternary compound carrying the prefix "hypo" contains one less atom of oxygen than the related "ite" compound:* $KClO_2$, potassium chlorite, and KClO, potassium hypochlorite.

It should be noted that the existence of atoms and their combination to form molecules of compounds was first postulated by John Dalton in 1803. The complete story of the development of the atomic theory and the concept of molecules is very interesting but is too long to be told in a short textbook.

1.16 Combining capacity. Valence. Examination of the formulas in Table 1.3 raises certain questions. In the compounds HCl, H_2O, NH_3, and CH_4 why does 1 atom of chlorine combine with 1 atom of hydrogen while 1 oxygen atom combines with 2 hydrogen atoms, 1 nitrogen atom with 3 hydrogen atoms, and 1 carbon atom with 4 hydrogen atoms? Why do sodium and chlorine combine in the ratio of 1 atom

of sodium to 1 atom of chlorine (NaCl), while with magnesium the ratio is 1 to 2 ($MgCl_2$), with aluminum 1 to 3 ($AlCl_3$), with carbon 1 to 4 (CCl_4), and with phosphorus 1 to 5 (PCl_5)? Why does oxygen combine with magnesium, calcium, zinc, and mercury in the ratio of 1 atom of oxygen to 1 atom of metal (MgO, CaO, ZnO, HgO) but with hydrogen and silver in the ratio of 1 atom of oxygen to 2 atoms of the other element (H_2O, Ag_2O)? These questions can be answered by postulating that, in any compound, the atoms are attached to or attracted to each other by bonds of some sort and that each element is provided with a definite number of bonds with which it can attach itself to other elements. The number of bonds determine the *combining capacity* or *valence* of the element. The hydrogen atom is selected as a standard of reference and is assumed to have 1 bond, or a valence of 1. Because 1 atom of hydrogen combines with 1 atom, respectively, of fluorine, chlorine, bromine, and iodine (HF, HCl, HBr, HI) each of these elements must have a valence of 1. Two atoms of hydrogen combine with 1 atom of oxygen (H_2O); therefore the oxygen atom must have a valence of 2. Three atoms of hydrogen combine with 1 atom of nitrogen (NH_3); therefore the nitrogen atom must have a valence of 3. Four atoms of hydrogen combine with 1 atom of carbon (CH_4); therefore the carbon atom must have a valence of 4. Since chlorine has a valence of 1 because it forms the compound HCl, the valence of sodium in NaCl must also be 1. Likewise the valence of K in KCl is 1, of Cu in $CuCl_2$ is 2, of Mg in $MgCl_2$ is 2, of Zn in $ZnCl_2$ is 2, of Al in $AlCl_3$ is 3, of C in CCl_4 is 4, and of P in PCl_5 is 5. Having concluded, from the formulas HF, HBr, and HI that F, Br, and I all have valences of 1, we can conclude from the formulas NaF, KI, and $CaBr_2$ that Na and K have valences of 1, while Ca has a valence of 2. We can conclude from the formula H_2SO_4 that the sulfate radical (SO_4), taken as a complete unit, has a valence of 2. It is therefore to be expected that copper, which has a valence of 2 (from $CuCl_2$), will combine with the sulfate radical in the 1 to 1 ratio represented by the formula $CuSO_4$ and that sodium, with a valence of 1 (from NaCl) will combine with the sulfate radical in the 2 to 1 ratio represented by the formula Na_2SO_4. Because the formula for hydrogen nitrate is HNO_3, the nitrate radical (NO_3) must have a valence of 1. Likewise, the formula H_2CO_3 for hydrogen carbonate gives the carbonate radical (CO_3) a valence of 2. From the formula NaOH for sodium hydroxide we deduce that the hydroxide radical OH has a valence of 1.

On the basis of what has been stated above we can say that the *valence of an element represents the number of atoms of hydrogen or their equivalent with which 1 atom of the element will combine.*

Table 1.4 lists the valences of some common elements and radicals. With the aid of this table one can determine the formulas of the compounds that would be formed by the combination of various pairs of substances. Thus zinc carbonate would be $ZnCO_3$ because both zinc and the carbonate radical have valences of 2.

TABLE 1.4

VALENCES OF SOME COMMON ELEMENTS AND RADICALS

Element	*Symbol or formula*	*Valence*	*Radical*	*Symbol or formula*	*Valence*
Hydrogen	H	1	Acetate	$C_2H_3O_2$	1
Oxygen	O	2	Bromide	Br	1
Potassium	K	1	Carbonate	CO_3	2
Sodium	Na	1	Chlorate	ClO_3	1
Calcium	Ca	2	Chloride	Cl	1
Magnesium	Mg	2	Hydroxide	OH	1
Aluminum	Al	3	Iodide	I	1
Zinc	Zn	2	Nitrate	NO_3	1
Iron	Fe	3, 2	Oxide	O	2
Lead	Pb	2	Phosphate	PO_4	3
Copper	Cu	2	Sulfate	SO_4	2
Mercury	Hg	2	Sulfide	S	2
Silver	Ag	1	Sulfite	SO_3	2
Carbon	C	4	Ammonium	NH_4	1
Phosphorus	P	5			
Sulfur	S	4, 6, 2			

The formula for zinc chloride would be $ZnCl_2$ because the valence of the chloride radical is 1. The total Cl valence must equal the total zinc valence. Thus ZnCl would be wrong because there would be 2 zinc bonds and only 1 chloride bond. *To be correct a formula must leave no unsatisfied valence bonds.*

The formula for zinc phosphate would be $Zn_3(PO_4)_2$. In deriving this formula it should again be noted that there must never be any unsatisfied valence bonds. The formula $ZnPO_4$ would be incorrect; since zinc has a valence of 2, while the PO_4 radical has a valence of 3, there would be 1 unsatisfied phosphate valence bond. The formula Zn_2PO_4 is also incorrect because there would be 4 zinc bonds and only 3 phosphate bonds. By taking 3 atoms of zinc and 2 phosphate radicals there will be 6 zinc bonds and also 6 phosphate bonds. Note that 6, representing the number of valence bonds provided by each part of the compound, is the least common multiple of 2, the valence of Zn, and 3, the valence of PO_4.

It follows from what has been stated above that, to demonstrate its

valence or combining capacity, an element must be combined with another element or radical. Therefore every free element has a valence of zero.

1.17 Calculations from the chemical formula. Because the chemical formula represents the definite and unchanging composition of a compound it can be used in making the following calculations:

1. *The formula weight or the molecular weight of the compound.* As already explained in Section 1.14, the formula weight is simply the sum of the atomic weights of the atoms represented by the formula. If the true chemical formula is known, the formula weight is also the molecular weight.

2. *The per cent of each element in the compound.* (This calculation can be made by using either a true chemical formula or an empirical formula.) Suppose, to illustrate, we wish to calculate the per cent of iron and oxygen, respectively, in iron oxide, Fe_2O_3. Per cent means "parts per 100 parts." What we want to calculate, then, is the parts by weight of iron and of oxygen in 100 parts by weight of Fe_2O_3. The formula Fe_2O_3 tells us that the compound is made up of iron and oxygen in the ratio of 2 atoms of iron to 3 atoms of oxygen. The formula weight is 159.70, and is obtained by adding the weights of the constituent atoms.

$$\begin{aligned} 2\,\text{Fe} &= 2 \times 55.85 = 111.70 \\ 3\,\text{O} &= 3 \times 16.00 = \underline{\ 48.00} \\ &\text{formula weight} = 159.70 \end{aligned}$$

This means that the weight of the iron is to the weight of the Fe_2O_3 as 111.70 is to 159.70, and the weight of the oxygen is to the weight of Fe_2O_3 as 48.00 is to 159.70; and these ratios apply whether we have a pinch of Fe_2O_3 or a large mass, whether we have 1 g or 159.7 g or 100 g or 25 g or 50 lb or 60 tons of Fe_2O_3. Stated differently it means that the fraction 111.70/159.70 represents that fractional part of any weight of Fe_2O_3 which is iron, and the fraction 48.00/159.70 represents that fractional part of any weight of Fe_2O_3 which is oxygen. In 100 parts by weight of Fe_2O_3 we will then have

(a) $\dfrac{111.7}{159.7} \times 100$ parts by weight = 69.9 parts by weight of iron

(b) $\dfrac{48.0}{159.7} \times 100$ parts by weight = 30.1 parts by weight of oxygen

Expressing this as per cent rather than parts by weight, we have

(c) $\frac{111.7}{159.7} \times 100\% = 69.9\%$ of iron

(d) $\frac{48.0}{159.7} \times 100\% = 30.1\%$ of oxygen

We can if we wish express this in the form of a proportion.

(e) $$\frac{111.7 \text{ parts by weight of iron}}{159.7 \text{ parts by weight of } Fe_2O_3} = \frac{x \text{ parts by weight of iron}}{100 \text{ parts by weight of } Fe_2O_3}$$

Solving this equation by transposition, we get

(f) $$\frac{111.7 \text{ parts by weight of iron}}{159.7 \text{ parts by weight of } Fe_2O_3} \times 100 \text{ parts by weight of } Fe_2O_3 = 69.9 \text{ parts by weight of iron}$$

Note that equation (f), which is the final equation that we get when we solve by proportion, is exactly the same as the equation, (a) or (c), that we use when we solve by the so-called *factor method* or *fraction method*. We can generalize what has been stated above and say that

(g) $$\% \text{ of element A in compound X} = \frac{\text{atomic weight of atoms of A in X}}{\text{formula weight of X}} \times 100\%$$

Since this solution requires only that we know the *ratio* of the weight of each constituent element to the weight of the compound it is obvious that either the empirical formula or the true chemical formula can be used.

3. *The weight of an element in a specific weight of its compound or the weight of compound which will contain a specific weight of the element.* (This calculation can be made by using either a true chemical formula or an empirical formula.) Suppose instead of being asked to solve for the per cent of iron in Fe_2O_3 we are asked to determine how many grams of iron there are in 25.0 g of Fe_2O_3. We will proceed exactly as we did in determining the per cent of iron in Fe_2O_3, except that in this case we will be dealing with 25 g of Fe_2O_3 rather than 100% or 100 parts by weight. Equation (a) will then be

$$\frac{111.7 \text{ g of iron}}{159.7 \text{ g of } Fe_2O_3} \times 25.0 \text{ g of } Fe_2O_3 = 17.5 \text{ g of iron}$$

Any desired weight of Fe_2O_3 can be used instead of 25.0 g.

If the problem is solved by proportion, equation (e) becomes

$$\frac{111.7 \text{ g of iron}}{159.7 \text{ g of } Fe_2O_3} = \frac{x \text{ g of iron}}{25.0 \text{ g of } Fe_2O_3}$$

and $$\frac{111.7 \text{ g of iron}}{159.7 \text{ g of } Fe_2O_3} \times 25.0 \text{ g of } Fe_2O_3 = 17.5 \text{ g of iron}$$

The weight need not necessarily be expressed in grams. Any unit of mass such as pounds or tons can be used because, as has been emphasized, the formula Fe_2O_3 tells us that 159.70 *parts by weight* of Fe_2O_3 contain 111.70 *parts by weight* of iron.

Suppose we are asked to solve the problem: How many grams of Fe_2O_3 will contain 40.0 g of iron? We go about it exactly as we did in the previous problem except that we now note that the ratio of the weight of the iron oxide to the weight of the iron that it contains is

$$\frac{159.70 \text{ parts by weight of } Fe_2O_3}{111.70 \text{ parts by weight of iron}} \quad \text{or} \quad \frac{159.70 \text{ g of } Fe_2O_3}{111.70 \text{ g of iron}}$$

That means that the weight of the Fe_2O_3 is 159.70/111.70 times the weight of the iron which it contains. Therefore

$$\text{weight of } Fe_2O_3 = \frac{159.70 \text{ g of } Fe_2O_3}{111.70 \text{ g of Fe}} \times 40.0 \text{ g of Fe} = 57.2 \text{ g of } Fe_2O_3$$

The problem can be solved by setting up the proportion

$$\frac{159.70 \text{ g of } Fe_2O_3}{111.70 \text{ g of Fe}} = \frac{x \text{ g of } Fe_2O_3}{40.0 \text{ g of Fe}}$$

$$\frac{159.70 \text{ g of } Fe_2O_3}{111.70 \text{ g of Fe}} \times 40.0 \text{ g of Fe} = 57.2 \text{ g of } Fe_2O_3$$

Note, in this last equation, that grams of Fe in the numerator is canceled by grams of Fe in the denominator; the answer is therefore *57.2 g of* Fe_2O_3. It is important in solving problems to label all terms and specify the exact units in which the numbers are expressed.

4. *For gaseous substances, the weight of any volume or the volume of any weight of the gas at any temperature and pressure.* (This calculation can be made only if the true chemical formula is known.) The details of this type of calculation will be discussed in Chapter 2.

1.18 Calories. Centigrade and Fahrenheit temperature scales. We learned in Section 1.11 that when elements combine to form compounds, energy, usually in the form of heat, is liberated or absorbed. The unit that is used to represent *quantity* of heat energy is the *calorie; a calorie is the quantity of heat required to raise the temperature of 1 gram of water 1 degree centigrade.* The easiest and most commonly employed way to decide whether or not heat energy is given off in the course of a chemical reaction is to note whether or not the *temperature* of the reacting material rises; the greater the amount of heat evolved, the hotter it

gets. The thermometers used to measure temperature in the laboratory are graduated in degrees centigrade; most household thermometers are graduated in degrees Fahrenheit. The fixed points on both scales are the freezing point and boiling point of water. On the centigrade scale the freezing point of water is 0° and the boiling point is 100°; the space between the fixed points is divided into 100 units, and the space above 100° and below 0° is divided into the same size units (see Figure 1.5). On the Fahrenheit scale the freezing point of water is 32° and the boiling point is 212°; the space between the fixed points is divided into 180 units, and the space above 212° and below 32° is divided into the same size units. Since the space between the freezing point and boiling point of water is divided into 100 degrees on the centigrade scale, and 180 degrees on the Fahrenheit scale, it follows that 100 centigrade degrees must represent the same temperature change as 180 Fahrenheit degrees. That means that 1 centigrade degree is equal to 1.8 Fahrenheit degrees; or, expressing it in fractional form, 1 centigrade degree is equal to $\frac{9}{5}$ Fahrenheit degrees, and 1 Fahrenheit degree is equal to $\frac{5}{9}$ centigrade degree. Conversion of temperature units from centigrade to Fahrenheit or from Fahrenheit to centigrade is often necessary. Such conversion can be accomplished in the manner illustrated by the following examples:

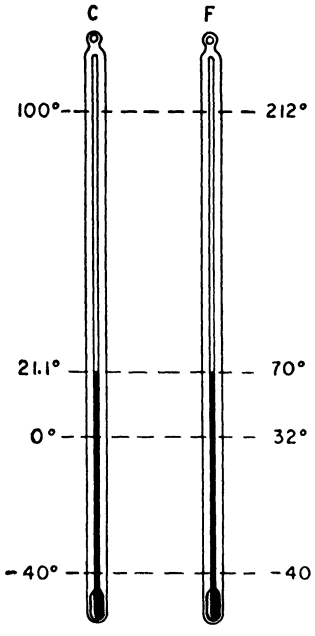


Figure 1.5. A comparison of centigrade and Fahrenheit temperatures.

(a) Let us convert 144°F to centigrade. To express it in °C we should note that 144°F is (144 − 32) or 112° above the freezing point of water. Since 1 Fahrenheit degree is equal to $\frac{5}{9}$ centigrade degree, 112 Fahrenheit degrees must be equal to $112 \times \frac{5}{9}$, or 62.2 centigrade degrees. Since the freezing point of water is 0°C, 62.2 centigrade degrees above the freezing point of water will be 62.2°C. Note that in converting the Fahrenheit reading to centigrade, we subtracted 32° from the Fahrenheit reading and multiplied the result by $\frac{5}{9}$. That is,

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

(b) Let us convert 80°C into °F. Now 80°C is 80 centigrade degrees above the freezing point of water. Since 1 degree C equals $\frac{9}{5}$ degrees F, 80°C will be $\frac{9}{5} \times 80$, or 144 Fahrenheit degrees above the freezing point of water. But the freezing point of water on the Fahrenheit scale is 32°. Therefore we must add 32 to our 144 to get the actual Fahrenheit temperature, 176°F. Putting what was done in the form of a formula, we get

$$F = \frac{9}{5}C + 32$$

1.19 The objectives of chemistry. Having been introduced to some of the basic concepts of chemistry we are prepared to understand the meaning of the statement that the objectives of chemistry as a science are:

1. *To observe:*

(a) Types and classes of matter. The chemist notes distinctive characteristics, identifying properties, similarities, and differences in matter.

(b) Changes in matter. These changes, called chemical reactions, involve changes in (1) the identity of matter, and (2) the energy content of matter.

2. *To explain* what is observed and to systematize these explanations in terms of

(a) Theories
(b) General principles
(c) Laws

3. *To use* the observations, facts, theories, general principles, and laws to man's advantage in:

(a) Producing desired changes, desired products
(b) Predicting new changes

As one proceeds with the study of chemistry, hundreds of examples illustrating the attainment of these objectives will be met. A simple case will serve as an illustration at this point:

The chemist *observes* that iron has certain characteristic properties. As a result of this observation of properties iron has attained wide *use* as a structural material. But the chemist observes also that iron rusts, and he *accounts for* and *explains* the rusting process by noting that it takes place only in the presence of air and moisture. To prevent rusting he keeps the iron dry or covers it with a coating of paint to keep out air and moisture. Having noted that exclusion of air will prevent rusting of iron, he concludes that it should prevent other deteriorative processes. This conclusion is put to practical use in the preservation of foods in airtight cans.

Questions and Problems

1. Define or describe each of the following and, where possible, give an illustration of each: matter; mass; weight; volume; liter; milliliter; cubic centimeter; gram; kilogram; milligram; density; physical properties; chemical properties; physical change; chemical change; chemical reaction; element; atom; atomic weight; gram-atomic weight; gram-atom; pound-atom; ton-atom; symbol; exothermic reaction; endothermic reaction; calorie; homogeneous; heterogeneous; compound; molecular weight; gram-molecular weight; formula weight; gram-formula weight; mole; formula; valence; binary compound; ternary compound; mixture.

2. Enumerate all the evidence which leads you to believe that a chemical compound is formed when the element magnesium is burned in a bottle of oxygen gas.

3. Describe, in detail, how the formula MgO is derived for the compound magnesium oxide.

4. The true chemical formula for the compound methane is CH_4. Show, by actual performance, the different calculations that can be made from this formula.

5. Give the valence of the element or radical set in boldface. **HBr**; **Ni**Br_2; **Ni**S; $\mathbf{K_2}S$; **K**I; **Cr**I_3; $\mathbf{Cr_2}O_3$; $\mathbf{Ag_2}O$; **Ag**Cl; **Na**Cl; **Na**$\mathbf{NO_3}$; $\mathbf{Mg}(NO_3)_2$; Mg$\mathbf{SO_4}$; $\mathbf{Al_2}(SO_4)_3$; Al$\mathbf{PO_4}$; $\mathbf{Zn_3}(PO_4)_2$; $Zn_2\mathbf{SiO_4}$; $\mathbf{Ca_2}SiO_4$; Ca$\mathbf{CO_3}$; **Cu**CO_3; Cu$\mathbf{SO_3}$; $\mathbf{Bi_2}(SO_3)_3$.

6. Using the valences that you have determined in Question 5, write the formula for each of the following: copper bromide; calcium iodide; magnesium sulfide; aluminum oxide; zinc chloride; aluminum bromide; bismuth oxide; potassium bromide; calcium nitrate; magnesium carbonate; sodium phosphate; silver sulfite; chromium silicate; zinc sulfate.

7. Calculate the formula weight of ZnO; of Fe_2O_3. How many grams of O are there in 150 g of ZnO? In 200 g of Fe_2O_3?

8. Calculate the per cent of S in H_2SO_4.

9. Sixty grams of Mg were completely burned. How many grams of MgO were formed?

10. Calculate the weight of 3 moles of CH_4; of 2 gram-atoms of P.

11. Ten grams of a pure compound contained 3.65 g of K, 3.33 g of Cl, and 3.02 g of O. Calculate its empirical formula.

12. A compound contains 29.1% Na, 40.5% S, and 30.4% O. Calculate its empirical formula.

13. How many individual atoms are there in 10.00 g of Mg?

14. Calculate the weight in grams of 4.00×10^{22} atoms of Ag.

15. How many individual molecules are there in 20 g of CH_4?

16. Calculate the weight in grams of 1.00×10^{23} molecules of CO_2.

17. How many pounds of S are combined with lead in 80 lb of PbS?

18. Now many tons of pure quartz (SiO_2) would contain 5 tons of Si?

19. Express the following centigrade temperatures in degrees Fahrenheit: 0°C; 100°C; 12°C; 200°C; −10°C; −40°C.

20. Express the following Fahrenheit temperatures in degrees centigrade: 32°F; 212°F; 0°F; 98°F; −40°F; −100°F.

21. A cube of solid exactly 4 cm on each edge weighed 251 g. Calculate the density of the solid.

22. A liquid has a density of 1.21 g/cc. What volume of the liquid will weigh 250 g?

CHAPTER 2

Gases, Liquids, Solids

Note to instructor: In this and succeeding chapters more comprehensive or advanced material is printed in smaller type. This material can be omitted without serious effect on the understanding of topics that follow.

2.1 A comparison of gases, liquids, and solids. We all know in a general way what is meant by the terms "gas," "liquid," and "solid." Air is a gas. We know that it is a form of matter because, when pumped into an automobile tire, it can support the weight of a heavy load, and when it moves at a rapid rate, as in a wind, it exerts a lot of force. We know that it must be extremely fluid because we can move through it with ease, much as if there were nothing there, and it flows out of a punctured tire very quickly. We know that it will distribute itself evenly throughout the entire volume of any container in which it is placed because when we blow air into a tire every part of the tire will support the weight of the car or truck.

Water is a liquid. It can be poured and it quickly takes the shape of the glass or pitcher in which it is placed. In contrast with air, however, it does not distribute itself evenly throughout the entire volume of the container in which it is placed. If we put a pint of water in a quart bottle we will find that the water will rest in the lower half of the bottle; there will be no liquid in the upper half of the bottle.

Iron is a solid. It is a rigid mass, it can not be poured like water, it will not flow, and it will not take the shape of the vessel in which it is placed.

We know, furthermore, that when liquid water is cooled to 0°C (32°F) it freezes and becomes solid ice, and when heated to 100°C (212°F) it boils and changes into gaseous steam. If the ice is heated it melts and becomes liquid water again; likewise, if the steam is cooled it changes back to water. This means that one and the same substance can, under the right conditions, exist either as a gas, a liquid, or a solid. Since water does not lose its identity when it is frozen to ice and melted back to water again or boiled into steam and condensed back to water again, the changes from water to ice, water to steam, ice to water, and steam to water must be *physical changes* rather than chemical changes.

Summarizing, we can say that

a *gas* is fluid, distributes itself uniformly throughout any container in which it is placed, and takes the shape of the container;

a *liquid* is fluid and takes the shape of the container in which it is placed but does not distribute itself uniformly throughout the container;

a *solid* is rigid, does not flow, and does not take the shape of the container. Under proper conditions many substances can exist as a gas, a liquid, or a solid.

2.2 The kinetic theory. Suppose we could equip ourselves with supermicroscopic eyes with which to see the detailed structures of gases, liquids, and solids. Looking first at a gas, a liter of steam for example, we would, it is believed, observe millions of individual molecules of H_2O flying around in the space inside the liter container. If we watched carefully we would observe some molecules moving a little faster than others and some moving a little slower but the bulk of them would be moving at about the same speed. The void space between H_2O molecules is very large compared with the actual space occupied by the individual molecules. A gas, we observe, is, in reality, a lot of space with many molecules flying around in it. If we were to heat the steam we would observe that the molecules move faster, if we cool it they move more slowly.

As we cool the steam the molecules move slower and slower. Finally, at 100°C (212°F) we observe that groups of the slowest molecules get together and condense to form drops of liquid water. Within the drop of liquid the H_2O molecules move about continuously. If the cooling is continued the steam is all condensed. If we continue cooling the liquid water we observe that the motion of the H_2O molecules becomes more sluggish. Finally, at 0°C (32°F) groups of H_2O molecules are observed to orient themselves into definite, rigid masses of solid ice crystals. If the cooling is continued, the entire mass of liquid water is changed into solid ice crystals. If we were to repeat the experiment with different samples of steam we would observe that the ice crystals always form in the same crystal pattern.

We could repeat the experiment with any number of available gaseous substances and we would find exactly the same series of changes taking place.

The concept cited above, that all gases, liquids, and solids are made up of molecules, that in a gas the molecules are moving about freely, that in a liquid they are moving about much less freely, while in a solid they are oriented in a definite rigid crystalline pattern, is referred to as the *kinetic-molecular theory of matter*. Evidence in support of the

kinetic-molecular theory and behaviors that result from the unique character of gases, liquids, and solids will be presented in the remainder of this chapter.

2.3 Diffusion of gases. Because a gas is made up of many freely moving molecules it will move into a space already occupied by other gaseous molecules. This movement of a substance into space already occupied by another substance is called *diffusion*. To illustrate, if a small quantity of brown bromine gas is placed in the bottom of a cylinder of air and the latter is closed by covering with a glass plate and allowed to stand undisturbed, the brown color of the bromine will slowly distribute itself through the cylinder. Eventually the gas in the cylinder will be uniformly light brown in color, indicating that the bromine has spread itself evenly through the air in the cylinder. If the diffusion experiment with bromine were repeated at different temperatures one would observe that as the temperature increases the rate of diffusion increases. The experimental facts of diffusion just cited lend strong support to the theory that gases are made up of molecules in a state of continuous motion, and that the rate of motion increases as the temperature increases.

2.4 Influence of pressure on the volume of a gas. Boyle's law. If pressure is applied to a gas its volume decreases. A common example to illustrate this is the fact that if you apply pressure with your hand or foot to a basketball or football it will be dented because the air inside the ball has been compressed. As soon as the pressure is released the dent will expand and the ball will take its regular shape. As the pressure increases, the volume of the gas decreases; this is an *inverse ratio*, one increasing, the other decreasing. It can be shown by actual experimentation that at constant temperature, if the pressure on a certain volume of gas is doubled the volume will be reduced to one-half its original volume. As illustrated in Figure 2.1, if the volume of a gas in a cylinder is 1000 cc when the total pressure upon it is 50 lb, the volume will be reduced to 500 cc when the total pressure is 100 lb, and will increase to 2000 cc if the total pressure is reduced to 25 lb. This means that *at constant temperature the volume of a gas is inversely proportional to the pressure*. This fact, originally observed by Robert Boyle, is known as *Boyle's law*.

Boyle's law may be expressed by the formula

$$\frac{V_1}{V_2} = \frac{P_2}{P_1} \tag{1}$$

in which V_1 is the volume at pressure P_1, and V_2 is the volume at pressure P_2.

Pressure is commonly expressed in units of millimeters of mercury. To say that a gas is under a pressure of 750 mm of mercury means that it is under the pressure that would be exerted by a column of mercury 750 mm high. The basis for expressing pressure in units of millimeters

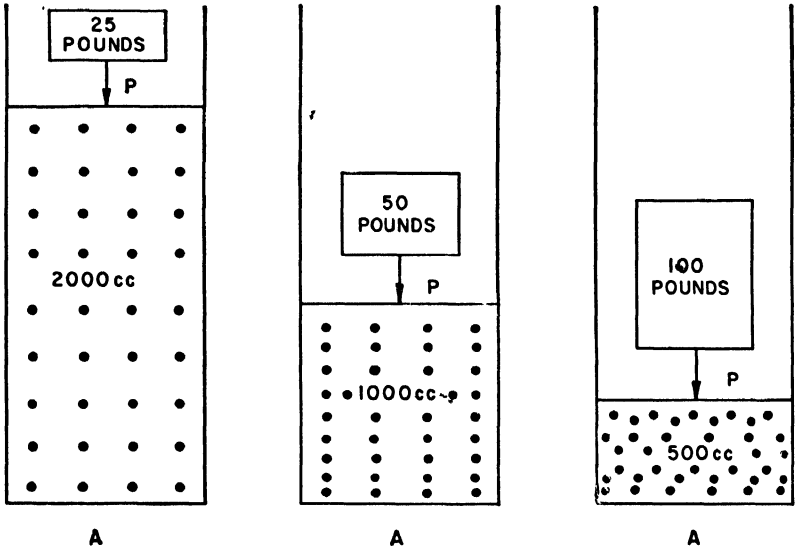


Figure 2.1. Influence of pressure on the volume of a gas. The cylinder, A, is fitted with a freely moving gas-tight piston, P. When the total pressure on the gas in the cylinder is 25 pounds its volume is 2000 cc. When the total pressure is doubled (increased to 50 lbs) the volume of the gas is reduced by one-half (to 1000 cc). When the pressure is again doubled (increased to 100 lbs) the volume of the gas is again reduced by one-half (to 500 cc). These results show that the volume of a mass of gas is inversely proportional to the pressure. Note that when the volume is reduced by one-half the same number of molecules are crowded into one-half the former volume; therefore, these molecules will strike the walls and piston twice as frequently as before and will therefore be able to exert twice as much pressure.

of mercury is the fact that a glass tube, sealed at its upper end and originally filled with mercury, inverted in a cup of mercury, as illustrated in Figure 2.2, has long been used as a barometer for measuring the pressure of the atmosphere, the so-called *barometric pressure.* When a tube of mercury is inverted in a cup of mercury in the manner shown in Figure 2.2, the mercury column will fall until it is at such a height that

its weight is just balanced by the weight of the column of air which is resting on the mercury in the outer part of the cup. If the mercury column comes to rest at a height h of 750 mm, it means that the pressure which the earth's column of air is exerting on the surface of the mercury in the open cup is the same as the pressure exerted by a column of mercury 750 mm high. At sea level the atmosphere exerts an average pressure throughout the year equal to that of a column of mercury 760 mm high. This average pressure of 760 mm of mercury is referred to as *standard pressure*. A pressure of 760 mm is called 1 *atmosphere*.

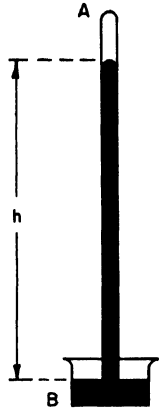


Figure 2.2. Simple barometer. When a tube A, filled with mercury, is inverted in a dish of mercury, B, the mercury in the tube will fall until its weight is counterbalanced by the weight of the column of air which is resting on the surface of the mercury in the dish. The height, h, at which the column comes to rest is the barometric pressure in units of millimeters of mercury. The average barometric pressure at sea level is 760 millimeters of mercury.

Boyle's law enables us to calculate the volume which a mass of gas will occupy at one pressure if we know what volume it occupies at another pressure, the temperature being constant meanwhile. Thus suppose a gas occupies a volume of 20 l at a pressure of 800 mm of mercury. What volume will it occupy if the pressure is reduced to 500 mm?

To solve we can either substitute in the Boyle's law formula, $V_2/V_1 = P_1/P_2$, or use a method in which we apply reasoning based on this formula. To solve by substitution we can let V_2 be the new volume that we are seeking (the *second volume* or *final volume*). Then P_2 is the pressure of 500 mm that is associated with V_2, and V_1 is 20 l (the *first volume* or *initial volume*), and P_1 is 800 mm (the *first pressure*). We will then get the result

$$\frac{V_2}{20\text{ l}} = \frac{800\text{ mm}}{500\text{ mm}} \tag{2}$$

$$V_2 = 20\text{ l} \times \frac{800\text{ mm}}{500\text{ mm}} = 32\text{ l} \tag{3}$$

Since the pressure has decreased, being reduced from 800 mm to 500 mm,

it is to be expected that the volume should increase; the answer therefore is sensible.

Equation (3) above gives us a clue to the second method. This equation tells us that the new volume, V_2, is the product of the old volume, 20 l, and the ratio of the two pressures, 800 and 500 mm.

(4) new volume = old volume × ratio of the two pressures

The question of how to set up the ratio of pressures, that is, what pressure to put in the numerator of the ratio and what one to put in the denominator, can easily be decided by a little common-sense reasoning. Since the pressure is reduced from 800 mm to 500 mm, the volume must increase. Therefore the answer must be greater than 20. To get an answer greater than 20 we must multiply the old volume, 20 l, by a number greater than 1. That means that the ratio of the two pressures must be greater than 1. Therefore 800 mm must fall in the numerator and 500 mm in the denominator. If 500 mm were placed in the numerator and 800 mm fell in the denominator, the fraction $\frac{5}{8}$ would be less than 1, and the answer would be less than 20.

The reverse of Boyle's law is obviously also true, namely, that *the pressure exerted by a mass of gas is inversely proportional to the volume which it occupies.*

The fact that a gas does exert pressure, and that at constant temperature this pressure is inversely proportional to the volume, is readily explainable in terms of the kinetic-molecular theory. The molecules of a gas are continually moving. At a constant temperature they move at a constant rate. Because they move they possess *energy of motion* or *kinetic energy.* When these moving molecules strike the walls of a containing vessel they exert pressure. The total pressure will be proportional to the number of times the walls are struck by molecules. If a definite number of molecules (a definite mass of gas) are contained in a vessel of a certain volume, they will strike the walls a certain number of times per second and will accordingly exert a certain pressure. If this same number of molecules is now crowded into a space one-half as large, they will strike the walls twice as many times per second and will therefore exert twice as much pressure.

The decrease in volume when the pressure on a mass of gas is increased at constant temperature can be accounted for in terms of the kinetic-molecular theory as follows: Suppose the gas occupies a volume of, let us say, 100 cc at a total outside pressure of 700 mm of mercury. The reason why the volume of the gas is exactly 100 cc is because when the molecules are confined in that amount of space they hit the walls often enough so that they exert a pressure equal to 700 mm of mercury

on each square centimeter of wall surface. The pressure of the gas molecules will then just counterbalance the pressure from the outside, and the volume will remain at 100 cc. Now suppose the pressure on the outside is increased to 800 mm. Since the pressure on the outside is now greater than the pressure which the molecules exert on the inside, the wall of the vessel, or the piston of the cylinder, will be pushed in and the molecules of gas will be crowded into a smaller space. Because they are crowded into a smaller space they will hit the walls more often and will thereby be able to exert more pressure. Soon they will be crowded into a small enough space so that they will hit the walls often enough to exert a pressure of 800 mm per square centimeter. The decrease in volume will then stop. The reason why a gas can be compressed at all is that there is such a lot of empty space between the molecules.

2.5 Influence of temperature on the volume of a gas. Charles's law. When a gas is heated at constant outside pressure it expands; when cooled it contracts. The reason why it expands when heated is that the molecules are caused to move faster, strike the walls oftener, and exert more pressure. As a result the pressure on the inside is greater than the constant pressure on the outside, and the wall of the containing vessel or the piston of the cylinder is pushed out and the volume of the gas is increased. As a result of this increase in volume the walls are struck less frequently. Finally the volume expands to the point where the impacts of faster moving warm molecules give a pressure just equal to that produced by the original impacts of slower moving cool molecules. The pressure will then be the same as the constant outside pressure, and the gas will stop expanding.

The exact relationship between volume and temperature can be derived as the result of an experiment somewhat as follows: Suppose a mass of helium gas is selected such that it has a volume of exactly 273 cc at 0°C at a constant pressure of about 760 mm. If the temperature is lowered to −1°C the volume is observed to have decreased to 272 cc. If lowered to −2°C the volume becomes 271 cc. Table 2.1 gives the volume that the gas would occupy at a large number of different temperatures. An examination of the data shows that a change of 1°C in the temperature changes the volume 1 cc, which is 1/273 of the volume at 0°C. If the volume were to continue to decrease, when cooled, at the same rate that it decreased from 0°C to −250°C, and if condensation to a liquid did not take place, then at −273°C it would be zero. The reason why a gas occupies space is that the molecules are moving. Therefore, one can conclude that the reason why a gas quits occupying space is that its molecules quit moving. The experiment would indicate that

this happens at about −273°C. This temperature, −273°C, is referred to as *absolute zero;* it is called absolute zero because at that temperature all molecular motion stops. It is generally expressed in degrees Kelvin (K). If −273°C is 0°K, then −100°C, which is 173 degrees warmer than −273°, would be 173°K, 0°C is 273°K and 273°C is 546°K. (See Figure 2.3.) If we note in Table 2.1 how the volume changes in relation to the absolute temperature expressed in degrees Kelvin, we see that at constant pressure *the volume of a given mass of gas is directly proportional to the absolute temperature.* This is *Charles's law.*

TABLE 2.1

VOLUME OF A MASS OF HELIUM GAS AT VARIOUS TEMPERATURES

Volume of the gas (cc)	*Temperature* (°C)	*Temperature* (°K)
546	273	546
275	2	
274	1	
273	0	273
272	−1	
271	−2	
270	−3	270
269	−4	
268	−5	
263	−10	263
253	−20	
200	−73	
173	−100	173
73	−200	
23	−250	
0 (extrapolated)	−273	0

Charles's law may be represented by the formula

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} \quad \text{or} \tag{5}$$

$$V_2 = V_1 \times \frac{T_2}{T_1} \tag{6}$$

in which T_2 and T_1 are the absolute temperatures, expressed in °K, at which the volumes V_2 and V_1, respectively, are measured. This formula enables us to calculate the volume which a given mass of gas will occupy at one temperature if we know what volume it occupies at some other temperature.

In applying the law it is important to note that

$$°K = °C + 273°.$$

0°C is referred to as *standard temperature.*

Suppose a mass of gas occupies a volume of 200 cc at 20°C. What volume will it occupy at 100°C, pressure remaining constant? As in the case of the Boyle's law problems that were discussed earlier, this problem can be solved either by substituting directly in the Charles's law formula or by a process of reasoning based on that formula. Solving by substitution, V_2 is the volume sought, the volume that the gas will occupy at 100°C (373°K); V_1 is 200 cc, and T_1 is 293°K (20°C + 273°). We then have

$$V_2 = 200 \text{ cc} \times \frac{373^\circ}{293^\circ} = 225 \text{ cc}$$

In solving by reasoning we note, according to equation (6), that

(7) new volume = old volume × ratio of the absolute temperatures

The choice as to which absolute temperature goes in the numerator and which in the denominator can readily be determined by common-sense reasoning. In the problem that we are solving we know that, since the temperature is being increased from 20°C to 100°C, the new volume will be larger than the old one. Therefore the number expressing the ratio of the absolute temperatures must be larger than 1, which means that 373°K goes in the numerator and 293°K in the denominator. Therefore

$$\text{new volume} = 200 \text{ cc} \times \frac{373^\circ}{293^\circ} = 225 \text{ cc}$$

Boyle's and Charles's laws will hold exactly only if a gas behaves as a *perfect gas*. A gas will behave as a perfect gas if the individual molecules of the gas take up no space and have no attraction for each other. Most gases are far from perfect; helium and hydrogen, however, come very close to being perfect. Therefore, neither Boyle's law nor Charles's law is exact. However, for the purposes of discussion in this course they will be assumed to be reasonably exact, and the simple formulas given above will be used in all calculations. Modified formulas which help compensate for the lack of perfection in a gas will be encountered in more advanced courses in chemistry.

2.6 The effect of change of temperature and pressure on the volume of a gas. The combined effect of change of temperature and pressure on the volume of a gas can be calculated by the use of the formulas

(8) new volume = old volume × ratio of pressures × ratio of absolute temperatures

(9) $$\frac{V_1P_1}{T_1} = \frac{V_2P_2}{T_2}$$

Formula (9) can be converted by transposition to the form

$$V_2 = V_1 \times \frac{T_2}{T_1} \times \frac{P_1}{P_2} \tag{10}$$

Formulas (9) and (10) can be derived as follows: Suppose the initial volume of a mass of gas is V_1 at pressure P_1 and temperature T_1. First, we will keep the temperature constant at T_1 and change the pressure from P_1 to P_2. This will change the volume to a value which we will call V_x. The Boyle's law formula yielding this intermediate volume will be

$$\frac{V_x}{V_1} = \frac{P_1}{P_2} \tag{11}$$

This, on transposition, gives

$$V_x = V_1 \times \frac{P_1}{P_2} \tag{12}$$

Next, we will keep the pressure on this volume, V_x, constant at P_2 and change the absolute temperature from T_1 to T_2. The new volume will be V_2, and the formula expressing the change will be

$$\frac{V_x}{V_2} = \frac{T_1}{T_2} \tag{13}$$

or

$$V_x = V_2 \times \frac{T_1}{T_2} \tag{14}$$

But the V_x in equation (12) is the same as the V_x in equation (14). Therefore

$$V_2 \times \frac{T_1}{T_2} = V_1 \times \frac{P_1}{P_2} \tag{15}$$

Transposing terms in equation (15) gives us

$$\frac{V_1 P_1}{T_1} = \frac{V_2 P_2}{T_2} \tag{9}$$

and

$$V_2 = V_1 \times \frac{T_2}{T_1} \times \frac{P_1}{P_2} \tag{10}$$

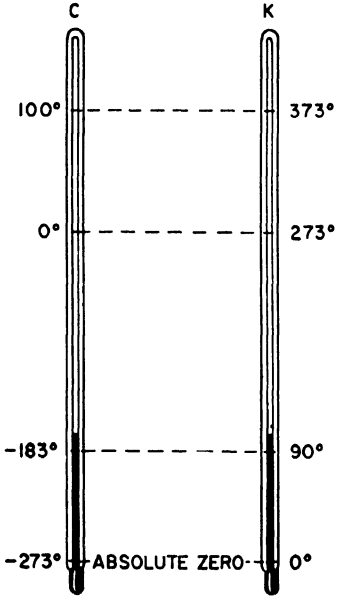


Figure 2.3. A comparison of centigrade and Kelvin temperatures. K = C + 273°.

Suppose we are given the problem: a mass of gas occupies a volume of 100 l at 12°C and 740 mm. What volume will it occupy at standard conditions of temperature and pressure (0°C and 760 mm)?

We can either substitute directly in formula (10) or we can use formula (8) and reason out the correct ratios of pressures and absolute temperatures. Applying either method, we will get

$$\text{new volume} = 100 \text{ l} \times \frac{273^\circ}{285^\circ} \times \frac{740 \text{ mm}}{760 \text{ mm}} = 93.3 \text{ l}$$

2.7 Molar volume of a gas. It has been determined, by experimental measurement, that 1 *mole* (1 gram-molecular weight) *of any gas occupies a volume of 22.4 liters at standard conditions* (STP, 0°C and 760 mm); 22.4 l is therefore referred to as the *molar volume* of a gas. It follows from this that *the weight in grams of 22.4 liters of any gas at STP is the gram-molecular weight of the gas.* The data upon which these conclusions are based are given in Table 2.2. The data in part (a) of the table show that 1 mole of any compound gas occupies 22.4 l at STP, and that the weight of 22.4 l of gas at STP is the weight of 1 mole (1 gram-

TABLE 2.2

MOLAR VOLUMES OF GASES

Formula of gas	*Gram-molecular weight*	*Weight in grams of 22.4 liters of gas at STP*
	(a) Compound gases	
CO_2	44 g	44 g
HCl	36.5 g	36.5 g
H_2S	34 g	34 g
HBr	81 g	81 g
CH_4	16 g	16 g
CO	28 g	28 g
HF	20 g	20 g
HI	128 g	128 g
C_2H_6	30 g	30 g
SO_2	64 g	64 g
	(b) Elementary gases	
O_2	32 g	32 g
H_2	2 g	2 g
N_2	28 g	28 g
Cl_2	71 g	71 g
F_2	38 g	38 g
Br_2	159.8 g	160 g
I_2	253.8 g	254 g
He	4 g	4 g
Ne	20.2 g	20 g
A	39.9 g	40 g
Kr	83.7 g	84 g
Xe	131.3 g	131 g

molecular weight) of the gas. As indicated in part (b) of the table, oxygen, hydrogen, nitrogen, chlorine, fluorine, bromine, and iodine gases exist as diatomic molecules with formulas O_2, H_2, N_2, Cl_2, F_2, Br_2, and I_2, respectively. In each instance 1 mole of the gas consists of 2 gram-atoms of the element. Helium, neon, argon, krypton, and xenon, however, exist as monatomic molecules.

The question will arise, How do we account for the fact that 1 mole of every gas, regardless of its molecular weight, occupies the same volume at STP, 22.4 l? The answer lies in the concept, stated in Section 1.14, that 1 mole of any and every gas contains 6.023×10^{23} molecules. At a given temperature each gas molecule has the same average kinetic energy as every other gas molecule, and the 6.023×10^{23} molecules of one gas have the same total kinetic energy as 6.023×10^{23} molecules of every other gas; because they have the same total kinetic energy they will be able to occupy the same space, and this space turns out to be 22.4 l at STP.

Since Boyle's and Charles's laws apply equally to all gases, it must follow that if 1 mole of every gas occupies the same volume, 22.4 l at STP, it will also occupy the same volume, though of course not 22.4 l, at any fixed temperature and pressure. This leads to the conclusion that, *at the same temperature and pressure, equal volumes of all gases contain the same number of molecules*, and *at the same temperature and pressure, equal numbers of molecules of all gases will occupy the same volume.* These generalizations are referred to as *Avogadro's hypothesis*, after the scientist who first made them. The number 6.023×10^{23}, representing the number of molecules in 1 mole of any substance, is called the *Avogadro number* and is referred to by the letter N.

The fact that 1 mole (1 gram-molecular weight) of any gas occupies a volume of 22.4 l at STP enables us to calculate (a) the volume occupied by any weight of any gas and the weight in grams of any volume of any gas at any temperature and pressure provided we know the true chemical formula of the gas molecule, and (b) the molecular weight, and hence the chemical formula, of any pure gas provided we know the weight of a definite volume of the gas at some definite temperature and pressure. To illustrate suppose we solve the problem, Calculate the weight in grams of 12 l of CH_4 gas at STP. The molecular weight of CH_4 is 16. Therefore 22.4 l of CH_4 at STP weigh 16 g. We can then calculate the weight of 12 l either by multiplying 12 l by the factor $\frac{16 \text{ g}}{22.4 \text{ l}}$ or we can set up and solve a simple proportion. By the factor method the solution would be

$$12\text{ l} \times \frac{16\text{ g}}{22.4\text{ l}} = 8.6\text{ g}$$

Note that a fraction such as $\frac{16\text{ g}}{22.4\text{ l}}$ always represents a "value per one," in this case the number of grams per one liter. Obviously, if we multiply the number of liters by the number of grams in one liter we will get the total number of grams. Note that liters in the numerator will cancel liters in the denominator. The answer will then be in grams.

Solving the problem by proportion, we reason that if 16 g is the weight of 22.4 l, then X g will be the weight of 12 l. This reasoning is expressed, mathematically, by the notation

$$\frac{16\text{ g}}{22.4\text{ l}} = \frac{X\text{ g}}{12\text{ l}}$$

Solving, we get $12\text{ l} \times \frac{16\text{ g}}{22.4\text{ l}} = X\text{ g}, \qquad X = 8.6\text{ g}$

2.8 Densities of gases. Density has already been defined as mass per unit volume. In the case of gases the unit of volume is generally a liter; the density is then expressed in units of grams per liter. The unit of volume can be 22.4 l and the density will then be expressed in units of grams per 22.4 l. But we have just learned that 1 mole of any and every gas occupies a volume of 22.4 l at STP. Therefore at STP the density of any gas, expressed in units of grams per 22.4 l, will be equal numerically to its molecular weight. Thus at STP the density of CH_4 is 16 g/22.4 liters or 0.71 g/liter, of H_2S is 34 g/22.4 liters or 1.52 g/liter, and of O_2 is 32 g/22.4 liters or 1.45 g/liter.

By applying the combined gas law formula we can calculate what volume a mole of gas will occupy at any temperature and pressure; knowing the volume and mass (which will not change) we can then calculate the density at that temperature and pressure. Since all gases have the same molar volume (22.4 l) at STP, and since Boyle's and Charles's laws apply equally to all gases, it follows that *at any temperature and pressure the densities of two gases are to each other as their molecular weights.* To demonstrate the truth of this statement suppose we compare the densities of CH_4 and H_2S at STP and also at 12°C and 750 mm. At STP

$$\text{density of } CH_4 = \frac{16\text{ g}}{22.4\text{ l}}, \quad \text{density of } H_2S = \frac{34\text{ g}}{22.4\text{ l}}$$

$$\frac{\text{density of } CH_4}{\text{density of } H_2S} = \frac{\frac{16}{22.4}}{\frac{34}{22.4}} = \frac{16}{34} = \frac{\text{mol wt of } CH_4}{\text{mol wt of } H_2S}$$

At 12°C and 750 mm

$$\text{density of } CH_4 = \frac{16 \text{ g}}{22.4 \text{ l} \times \frac{760}{750} \times \frac{285}{273}}$$

$$\text{density of } H_2S = \frac{34 \text{ g}}{22.4 \text{ l} \times \frac{760}{750} \times \frac{285}{273}}$$

$$\frac{\text{density of } CH_4}{\text{density of } H_2S} = \frac{\dfrac{16}{22.4 \times \frac{760}{750} \times \frac{285}{273}}}{\dfrac{34}{22.4 \times \frac{760}{750} \times \frac{285}{273}}} = \frac{16}{34} = \frac{\text{mol wt of } CH_4}{\text{mol wt of } H_2S}$$

Obviously, it will not be necessary to memorize densities of gases; if we know the true chemical formula of the gas we can calculate the density at any temperature and pressure.

2.9 The gas law formula, $PV = nRT$. The combined gas law (Boyle's and Charles's) can be expressed by the formula $PV = nRT$, in which R is the so-called *gas constant* and n is the number of moles of gas. If 1 mole of gas is involved, $n = 1$, and the formula becomes $PV = RT$. This formula follows directly from the combined gas law equation, $PV/T = P_0V_0/T_0$, where V_0 is the volume, 22.4 l, which 1 mole of a gas will occupy at standard conditions, T_0 is standard temperature, 273°K, and P_0 is standard pressure, 760 mm or 1 atm. Since V_0, P_0, and T_0 are all constant, the term V_0P_0/T_0 is constant; it is the gas constant, R. Since $R = V_0P_0/T_0$ and $PV/T = P_0V_0/T_0$, then $PV/T = R$ and $PV = RT$. The value of R can be calculated by substitution in the formula

$$R = \frac{V_0P_0}{T_0}$$

If P_0 is 1 atm,

$$R = \frac{22.4 \text{ l} \times 1 \text{ atm}}{273°\text{K}} = 0.082 \frac{\text{l} \times \text{atm}}{\text{deg}}$$

If P_0 is 760 mm,

$$R = \frac{22.4 \text{ l} \times 760 \text{ mm}}{273°\text{K}} = 62.4 \frac{\text{l} \times \text{mm}}{\text{deg}}$$

Since R is calculated for 1 mole, the value for n moles will obviously be nR. Therefore $PV = nRT$, in which n is the number of moles of gas involved. The use of this formula may be illustrated by solving the problem: calculate the volume occupied by 20.0 g of H_2S gas at 20°C and 700 mm pressure.

V = the volume sought, $P = 700$ mm, $T = 293°\text{K}$

$$n = \frac{20.0}{34.1} \text{ mole (Since one mole of } H_2S \text{ weighs 34.1 g,}$$
20.0 g will be 20.0/34.1 mole.)

Substituting these values in the formula,

$$V = \frac{nRT}{P} = \frac{20.0}{34.1} \times \frac{62.4 \times 293}{700} = \frac{20.0 \times 62.4 \times 293}{34.1 \times 700} = 15.3 \text{ l}$$

2.10 Partial pressures of gases in a mixture. In a mixture of gases each gas will behave independently of the others; each gas in the mixture will exert the pressure which it would exert if it alone occupied the volume occupied by the mixture. Suppose, for example, $\frac{1}{2}$ mole of CH_4 gas (8 g or $\frac{6.023}{2} \times 10^{23}$ molecules) and $\frac{1}{2}$ mole of CO_2 gas (22 g or $\frac{6.023}{2} \times 10^{23}$ molecules) are placed in a 22.4 l container at 0°C. The mixture of two gases exerts a pressure of 760 mm. Since 1 mole of any gas will exert a pressure of 760 mm when it occupies a volume of 22.4 l at 0°C it follows that the $\frac{1}{2}$ mole of CH_4 will exert a pressure of only $\frac{1}{2}$ of 760 mm, or 380 mm, when it occupies a volume of 22.4 l, and the $\frac{1}{2}$ mole of CO_2 will also exert a pressure of only 380 mm. The total pressure being 760 mm, half of this pressure is sustained by the $\frac{6.023}{2} \times 10^{23}$ molecules ($\frac{1}{2}$ mole) of CH_4, and half by the $\frac{6.023}{2} \times 10^{23}$ molecules ($\frac{1}{2}$ mole) of CO_2. The pressure exerted by the CH_4 is called its *partial pressure;* the partial pressure of the CH_4 is thus 380 mm. The partial pressure of the CO_2 is also 380 mm. If the mixture had contained $\frac{3}{4}$ mole (75 mole per cent) of CH_4 and $\frac{1}{4}$ mole (25 mole per cent) of CO_2, the partial pressure of the CH_4 would have been 570 mm or $\frac{3}{4}$ (75%) of the total pressure, while the partial pressure of the CO_2 would have been 190 mm or $\frac{1}{4}$ (25%). From these illustrations we can conclude that *the partial pressure of a gas in a mixture is proportional to its mole per cent or mole fraction.* (By *mole fraction* we mean the fraction of the total number of moles in the mixture.) This is *Dalton's law.*

2.11 Graham's law of diffusion. We have already learned that, because a gas is made up of freely moving molecules, it has the ability to *diffuse* into a space already occupied by another gas. If the rates at which different gases diffuse are observed, it will be noticed that a light gas diffuses faster than a heavy one. Thus hydrogen gas, which has a density of 2 g/22.4 l, diffuses a great deal faster than does bromine,

whose density is 160 g/22.4 l. If the relative rates at which different gases diffuse are measured accurately it will be found that *the rates of diffusion are inversely proportional to the square roots of the densities of the gases.* This is *Graham's law of diffusion,* and may be represented by the formula

$$\frac{\text{rate of diffusion of gas A}}{\text{rate of diffusion of gas B}} = \frac{\sqrt{\text{density of gas B}}}{\sqrt{\text{density of gas A}}} \tag{16}$$

The rate of diffusion may be expressed in various units such as cubic centimeters per second, cubic centimeters per minute, and liters per hour. The density is commonly expressed in units of grams per 22.4 liters or grams per liter. In an actual laboratory experiment methane gas, CH_4, which has a density of 16 g/22.4 l at STP, diffuses about $1\frac{1}{2}$ times as fast as hydrogen chloride, HCl, whose density at STP is 36.5 g/22.4 l. If we substitute these two density values in equation (16) we obtain

$$\frac{R_{CH_4}}{R_{HCl}} = \frac{\sqrt{D_{HCl}}}{\sqrt{D_{CH_4}}} = \frac{\sqrt{36.5}}{\sqrt{16}} = \frac{6}{4} = 1\frac{1}{2}$$

This agrees with the results obtained by measuring the rates of diffusion experimentally.

As previously noted in Section 2.8, under the same conditions of temperature and pressure the densities of two gases are to each other as their molecular weights. Therefore molecular weight (M) can be substituted for density in the Graham's law formula regardless of the temperature and pressure, as long as each gas is measured at the same temperature and pressure. The formula then becomes

$$\frac{R_A}{R_B} = \frac{\sqrt{M_B}}{\sqrt{M_A}} \tag{17}$$

The Graham's law formula, (17), can be derived in the following manner: It has already been noted that, at the same temperature, the molecules of all gases have the same average kinetic energy. The kinetic energy of any moving body is equal to one-half the product of its mass and the square of its velocity.

(18) kinetic energy = $\frac{1}{2}$ mass $\times$ velocity^2 = $\frac{1}{2}mv^2$

(19) average kinetic energy of gas molecule A = average kinetic energy of gas molecule B

(20) $\text{KE of A} = \frac{1}{2}m_A v_A^2$

(21) $\text{KE of B} = \frac{1}{2}m_B v_B^2$

Combining equations (19), (20), and (21), we obtain

$$\frac{v_A^2}{v_B^2} = \frac{m_B}{m_A} \quad \text{and} \quad \frac{v_A}{v_B} = \frac{\sqrt{m_B}}{\sqrt{m_A}} \tag{22}$$

But v_A is the average velocity with which the molecules of A move, and v_B is the average velocity with which the molecules of B move. Since the rates at which molecules of A and B diffuse will obviously be proportional to their velocities, we can substitute R_A and R_B for v_A and v_B, respectively. Since m_B and m_A are the masses of molecules of A and B they obviously will be the molecular weights of A and B. Substituting these values in equation (22) gives us

$$\frac{R_A}{R_B} = \frac{\sqrt{M_B}}{\sqrt{M_A}} \tag{17}$$

2.12 Liquefaction of gases. If a gas is cooled, the molecules move more slowly and their kinetic energy decreases. This causes the volume to contract and brings the individual molecules closer together. If they are cooled enough, their kinetic energies may fall so low and they may get so close to each other that they are then pulled together by the force of intermolecular attraction. As a result the gas changes to a liquid; it *condenses* or is *liquefied*. Regardless how close the molecules of a gas are to each other they will not be pulled together to form a liquid until their kinetic energy has been reduced to a certain maximum value by lowering the temperature. The temperature to which a certain gas must be lowered before it can be liquefied is called the *critical temperature*, and the pressure that must be applied in order to produce liquefaction at the critical temperature is called the *critical pressure*. No gas can be liquefied at a temperature above its critical temperature. Below the critical temperature it is possible to liquefy a gas merely by compressing it sufficiently. For any gas, the farther it is cooled below its critical temperature the smaller the pressure required to cause liquefaction.

Each gas has its own specific critical temperature. For hydrogen the value is −239.9°C, for nitrogen −147.1°C, for oxygen −118.8°C, for ammonia 132.4°C, for sulfur dioxide 157.2°C, and for water 374.0°C. When nitrogen gas is cooled to −195.8°C, a pressure of 1 atm will condense it, but at its critical temperature a pressure of 33.5 atm is required. When water vapor is cooled to 100°C, a pressure of 1 atm will condense it, but at its critical temperature a pressure of 217.7 atm is nece sary.

2.13 Equilibrium between a liquid and its vapor. To learn exactly what goes on when a gas is liquefied, suppose we fill a cylinder, Figure 2.4a, with steam (water vapor) at some constant temperature, say 120°C, and gradually increase the pressure on the movable friction-

less piston B. As the pressure is increased the volume will decrease, and the H_2O molecules will get closer and closer to each other. At any particular moment the *average* distance between every pair of molecules will be the same, and the average energy of each molecule will be the same, but some pairs will be a little closer together than the average and some will have less energy than others. Finally, when the volume is reduced sufficiently some of the molecules will be so close to each other and of such low energy that they will be pulled together by the force of intermolecular attraction to form tiny drops of liquid water. As a result of this change of gas to liquid there will, momentarily, be fewer gas molecules *per unit volume* in the cylinder, and the distance apart of these remaining molecules will consequently be a little greater than before, too great in fact to allow them to be pulled together to form a liquid. Liquefaction will stop, momentarily. However, because there are now fewer gas molecules per unit volume, they will not exert so much pressure as before, not enough in fact to counterbalance the thrust on the piston. As a result the piston will be pushed in a little, the volume of the gas will be reduced, the gas molecules will get close enough together so that they can exert enough pressure to counterbalance the thrust on the piston, and also close enough together so that they will again change to liquid. If the constant pressure which was necessary to start liquefaction is kept applied to the piston and the temperature of the cylinder and its gas-liquid contents are kept constant at 120°C (by removing any heat that is given off) the above described cycle of changes will go on and on, more and more liquid water will accumulate, and less and less water vapor (gas) will remain. It is important to notice that during this time while the temperature is kept constant at 120°C the pressure required to continue the liquefaction remains the same.

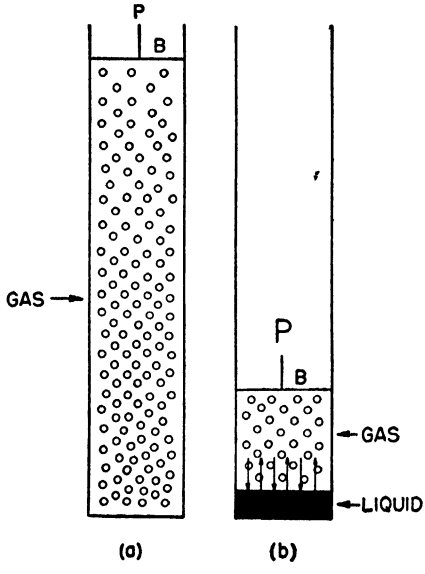


Figure 2.4. Liquefaction of a gas by increasing the pressure.

If we lock the piston in place when the cylinder contains the amount of gas (water vapor) and liquid (water) shown in Figure 2.4b and note

carefully with supermicroscopic eyes what is going on, we will observe that gas molecules keep right on condensing to form liquid, but for every molecule that changes from gas to liquid another molecule changes from liquid to gas. The process goes on and on without any letup. The *rate* at which gas is changing to liquid is exactly the same as the *rate* at which liquid is changing to gas. Because these two rates are the same, the process represents a *state of equilibrium* and *the liquid is said to be in equilibrium with its vapor*. The pressure which the gas molecules exert when they are in equilibrium with the molecules of liquid is called the *equilibrium vapor pressure* of the liquid.

If the pressure on the system is now increased momentarily by moving the piston down a bit, more vapor will condense until equilibrium is again established. This illustrates the *principle of Le Chatelier*, which states that *when a system in a state of equilibrium is subjected to a stress or strain a change will take place which will relieve that stress or strain.*

If the complete experiment is repeated any number of times at 120°C the pressure required to cause liquefaction, which is the vapor pressure of water at 120°C, will always be the same. As the temperature is lowered the vapor pressure (liquefaction pressure) decreases. At 100°C the equilibrium vapor pressure for water is 760 mm of mercury; at 90°C, 633.90 mm; at 80°C, 355.10 mm; at 50°C, 92.51 mm; and at 10°C, only 9.21 mm. Table 2.3 gives the vapor pressure of water at different temperatures from 0°C to 100°C.

TABLE 2.3

VAPOR PRESSURE OF WATER

Temperature (°C)	*Vapor pressure* (mm mercury)	*Temperature* (°C)	*Vapor pressure* (mm mercury)	*Temperature* (°C)	*Vapor pressure* (mm mercury)
0	4.58	22	19.83	40	55.32
5	6.54	23	21.07	45	71.88
10	9.21	24	22.38	50	92.51
11	9.84	25	23.76	55	118.04
12	10.52	26	25.21	60	149.38
13	11.23	27	26.74	65	187.54
14	11.99	28	28.35	70	233.70
15	12.79	29	30.04	75	289.10
16	13.63	30	31.82	80	355.10
17	14.53	31	33.70	85	433.60
18	15.48	32	35.66	90	525.76
19	16.48	33	37.73	95	633.90
20	17.54	34	39.90	100	760
21	18.65	35	42.18		

2.14 Boiling. Suppose, instead of starting with steam at 120°C and liquefying it by increasing the pressure as we did in the previous discussion, we place a quantity of pure water in the cylinder, Figure 2.5a, in such a manner that the piston fits right down on the surface of the water. The temperature at the start is 20°C, and the pressure on the water in the cylinder, represented by the weight of the piston plus the pressure of the atmosphere on the piston, is 760 mm of mercury. We will now gradually heat the water and cylinder and observe what happens. We will note that at the starting temperature, 20°C, as at all other temperatures, the molecules of the liquid water are continually moving around. As the temperature increases, the rate at which the

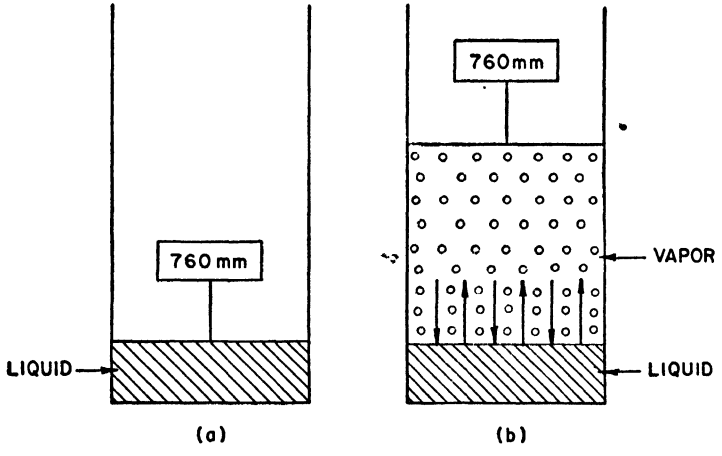


Figure 2.5. Boiling. Equilibrium between a liquid and its vapor.

liquid molecules move increases. Because the molecules are moving they have kinetic energy, and because they have kinetic energy they can exert pressure on the under side of the piston that fits down on the surface of the water. As long as the pressure which these moving water molecules exert is less than the 760 mm pressure with which the piston is pushing down on the surface they remain in the liquid state. When the temperature reaches 100°C the molecules are moving so fast that they have enough kinetic energy to exert a pressure of 760 mm of mercury per square centimeter of surface. That means that they can push the piston up, and in so doing, change from a liquid to a gas. When this happens the water is said to *boil;* the temperature at which this happens is called the *boiling point;* as long as the pressure in our experiment remains constant at 760 mm the water will keep on boiling at 100°C until all the liquid water has changed to steam. To change water from

the closely packed state of a liquid to the more highly dispersed state of a gas the molecules must do work, and to do this work they need energy. This energy they get in the form of heat from the burner or other heating device. If we would reduce the rate of heating in our experiment to the point where the rate of boiling is so slow that rising bubbles of steam are no longer perceptible we would then observe, with our supermicroscopic eyes, that molecules of H_2O vapor are changing back to liquid at the same rate that liquid H_2O molecules are changing to vapor (see Figure 2.5b). In other words, *at the boiling point the liquid is in equilibrium with its vapor*, and the pressure exerted by the vapor is the vapor pressure of its liquid at the boiling temperature. We can conclude therefore that *a liquid will boil when its vapor pressure is equal to the pressure which is being exerted on its surface* and *the boiling point of a liquid is that temperature at which its vapor pressure equals the outside pressure on its surface.* When a liquid boils in an open vessel the outside pressure which it must overcome is the pressure of the atmosphere. It must follow from the definition given above that *the boiling point changes when the outside pressure changes.* That fact is shown in Table 2.3 in which the temperatures are the boiling points of water at the indicated pressures. Quite obviously, when the boiling point of a liquid is given, the pressure must be specified. A liquid can be caused to boil by lowering the pressure as well as by raising the temperature.

The boiling points of different liquids differ greatly. At 760 mm water boils at 100°C, ethyl ether boils at 34.6°C, ethyl alcohol boils at 78.3°C, while mercury boils at 357°C. Liquids, such as ethyl ether and ethyl alcohol, which have low boiling points (high vapor pressures) are said to be *volatile*, while liquids with high boiling points possess low volatility.

Because a pure substance always boils at the same definite temperature when heated at a definite pressure, it can be identified by means of its boiling point. The boiling points of a great many chemical substances are listed in tables such as the *International Critical Tables.*

Because a liquid boils when its vapor pressure equals the outside pressure and because the vapor pressure of a pure liquid is constant at a given temperature, it follows that, if the outside pressure is constant, the temperature must remain constant during the boiling process. Turning up the heat of the burner speeds up the rate of boiling, but except for possible local superheating, does not raise the boiling temperature. The heat required to change a liquid to a vapor at its boiling point is called the *heat of vaporization;* it is usually expressed in units of calories per mole or calories per gram. The heat of vaporization of water is 539 cal per gram at 100°C. Since heat is absorbed when a

liquid changes to a vapor it must follow that this heat must be given off when the vapor condenses to a liquid. It is called *heat of condensation* and is equal, numerically, to the heat of vaporization. The process or cycle by which a liquid is changed to vapor by boiling and this vapor is in turn cooled and condensed back to a liquid is called *distillation* (see Figure 2.6).

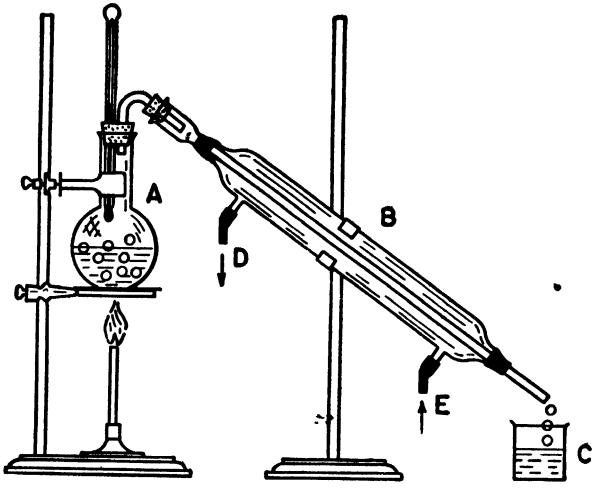


Figure 2.6. Distillation of a liquid. The liquid to be distilled is placed in flask *A* and heated to its boiling point. The vapor is condensed by the water-cooled condenser *B* and collects as a liquid in receptacle *C*. The cooling water for the condenser enters at *E* and leaves at *D*.

2.15 Evaporation of liquids. If a pure liquid is placed in an open dish out in the open air it will gradually disappear. An examination will reveal that the molecules of liquid have passed into the air where they exist in the form of gas molecules. This escape of molecules of liquid by their change to a gas is called *evaporation*. The more volatile a liquid, the more rapidly it evaporates. As the temperature increases, the rate of evaporation increases; this is in agreement with the fact that increase in temperature increases the vapor pressure of a liquid.

Suppose a quantity of pure water is placed in a cylinder filled with dry air and the piston is put into place, giving a setup such as that shown in Figure 2.7a. The total pressure on the air and water, represented by the sum of the piston and the pressure of the atmosphere is, let us say, exactly 760 mm of mercury, and the temperature is kept constant at 20°C. If we were to watch this system with supermicroscopic eyes, this is what we would observe. Gas molecules of H_2O would

immediately start escaping at a *definite rate* from the surface of the water, and this *definite rate of evaporation would continue* throughout the experiment. As soon as some molecules of H_2O were mixed with the air an occasional one would pop back into the liquid (see Figure 2.7b). As the number of molecules of H_2O vapor in the space above the liquid increases, the number of those that pop back into the liquid increases (see Figure 2.7c). Finally the rate at which H_2O molecules go back into

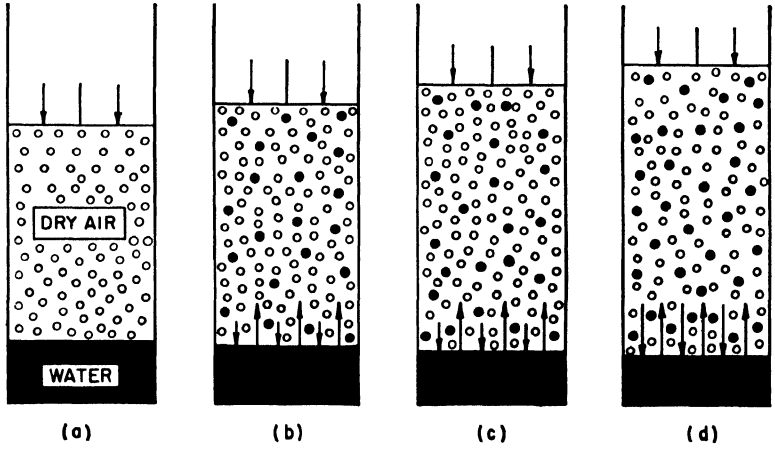


Figure 2.7. Evaporation of a liquid.

the liquid is exactly the same as the rate at which liquid molecules are evaporating. We now have a state of equilibrium, and the air above the surface of the water is said to be *saturated with water vapor*. If we could measure the pressure exerted by the H_2O vapor molecules we would find that it was exactly 17.54 mm. An examination of Table 2.3 shows that this is the vapor pressure of water at 20°C. While the state of equilibrium was being reached we would observe that the volume of the gas in the cylinder was slowly increasing until, at equilibrium, we would have the situation represented by Figure 2.7d. Once equilibrium is established the volumes of liquid and gas remain constant but we notice that the evaporation-condensation equilibrium process keeps right on going. We can conclude that *a liquid is in equilibrium with its saturated vapor.*

Suppose we now increase the temperature of the water and cylinder to 50°C. The rate of evaporation increases, as does the volume of the gas phase (air plus water vapor). Finally, equilibrium is again established; but the rate at which the molecules evaporate and condense is faster than at 20°C, and the per cent of H_2O molecules in the gas phase

is greater. If we continue increasing the temperature the per cent of H_2O molecules in the gas phase becomes greater and greater. Finally, at 100°C, the vapor pressure of the H_2O molecules equals the outside pressure of 760 mm, the piston is forced out of the cylinder, the H_2O gas molecules have swept all the air out of the cylinder, and we have only H_2O vapor in equilibrium with liquid water. The water is now boiling because it is in equilibrium with its pure vapor and its vapor pressure is equal to that of the outside pressure. Boiling is therefore a special case of equilibrium evaporation.

We noted that when equilibrium was established at 20°C the vapor pressure of the saturated water vapor was 17.54 mm. This, then, is the *partial pressure* of the water vapor. Since the total pressure was 760 mm, the partial pressure of the air in the gas mixture must have been 760 mm − 17.54 mm, or 742.46 mm. This is equivalent to saying that of the total pressure of 760 mm only 742.46 mm is being exerted on the air, while 17.54 mm is being exerted on the water vapor. Whenever a gas is collected over water the actual pressure on the gas is the observed outside pressure minus the vapor pressure of water at that temperature. Table 2.3 gives the vapor pressures for water.

If the partial pressure of the water vapor in contact with the surface of an evaporating liquid is kept low, by blowing a current of dry air over it, the rate at which water vapor molecules pop back into the liquid will be reduced. The result is that the net rate of evaporation is increased. That is why wet clothes dry better on a windy day.

The cooling which results from evaporation of a liquid may be accounted for as follows: in evaporation the molecules with the highest kinetic energy escape, leaving behind those of lower kinetic energy. Since the rate at which the molecules move, and hence their kinetic energy, increase with increase in temperature, it follows that the faster moving molecules, those with higher kinetic energies, are hotter than the slow-moving ones. Since the hotter molecules escape, the liquid that remains behind must be cooler because of its higher content of colder molecules.

2.16 Relative humidity. Water vapor gets into the air as a result of a variety of processes, one of which is evaporation from bodies of water. The extent to which atmospheric air is saturated with water vapor is referred to as *relative humidity*. If the air is absolutely saturated its relative humidity is 100%. If it contains only half as much water vapor as it is capable of holding, its relative humidity is 50%. The higher the temperature, the greater the vapor pressure of water, and hence the greater the amount of vapor that the atmosphere can

hold. Furthermore, the higher the temperature, the more rapidly water evaporates and the more quickly the vapor content of the air is built up. As a result, the air is damp and humid in hot summer weather but dry in cold winter weather. Table 2.3 tells us that if warm air of high humidity is cooled to a lower temperature it may reach a condition where it becomes saturated with water vapor. Further cooling will exceed this saturation point, and moisture will then condense as fog, as clouds, as dew on the surface of vegetation, or as condensed water on cold-water pipes, basement walls, and glasses containing cold water. When air is saturated with water vapor it is said to be at the *dew point*, this being the temperature below which further cooling will produce condensation or "*dew*."

2.17 Refrigeration. The fact that heat is absorbed when a liquid vaporizes (evaporates or boils) plus the facts that a liquid may be vaporized by lowering the pressure, while a vapor may be liquefied by increasing the pressure, are the bases for the operation of modern refrigeration systems. A gas with a fairly high critical temperature, a

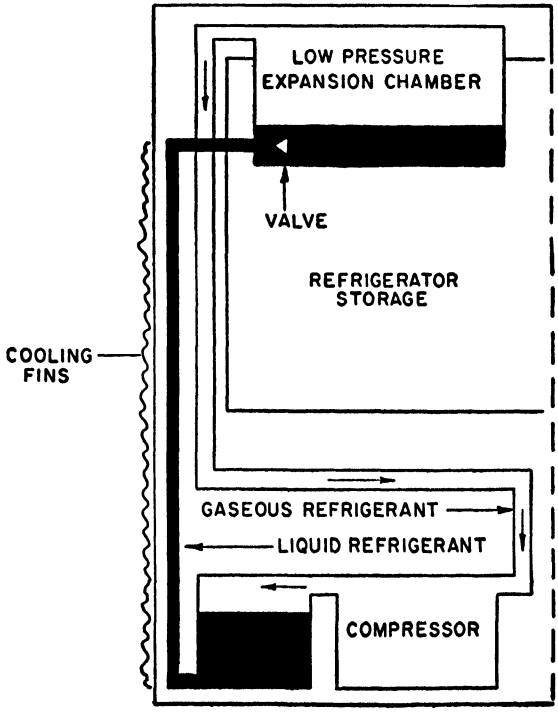


Figure 2.8. A refrigerator.

low boiling point, and a high heat of vaporization is liquefied by being compressed in the cylinder of a compression pump. The heat which is given off when the gas is liquefied is allowed to escape into the air; metal fins attached to the compressor help conduct the heat away. The liquid is allowed to pass from the compressor through a control valve into a chamber where the pressure is low enough so that the liquid will vaporize. This chamber surrounds the refrigeration storage space or, in large refrigeration systems, a tank of brine which can be circulated through the area to be refrigerated. The heat which is absorbed when the liquid vaporizes is taken up from the walls of the chamber, which in turn take it from the material stored in the refrigerator, or from the brine solution. The gas (vapor) then goes back to the compressor pump and the liquefaction-evaporation cycle is repeated. The refrigerator temperature can be controlled by regulating the pressure in the vaporization chamber and the rate at which liquid is allowed to pass into this chamber. The lower the pressure in the chamber and the more rapidly the liquid enters the chamber, the lower the refrigerator temperature. Figure 2.8 shows the layout for a refrigeration system, and Table 2.4 gives significant facts about gases commonly used in modern refrigeration systems. Ammonia, because of its extremely high heat of vaporiztion, is the most effective of the refrigerants listed and is used in most large commercial ice machines, cold storage plants, and refrigerator systems. However, its unpleasant odor and somewhat toxic character make it unsatisfactory for use in domestic refrigerators. Accordingly, the odorless, nontoxic Freon gases are now generally used in the latter units.

TABLE 2.4

PROPERTIES OF GASES USED IN REFRIGERATION

Gas	*Critical temperature*	*Boiling point* (at 760 mm)	*Heat of vaporization* (cal/g)
Ammonia (NH_3)	132.4°C	−33.3°C	309.9 (−10°C)
Dichlorodifluoromethane (Freon, CCl_2F_2)	111.5°C	−29.8°C	38.6 (−15°C)
Methyl chloride (CH_3Cl)	143.0°C	−23.7°C	98.5 (−10°C)
Sulfur dioxide (SO_2)	157.2°C	−10.0°C	91.2 (0°C)

2.18 Specific heat of a liquid. When the temperature of a liquid is increased, the molecules are caused to move more rapidly and their total energy is increased. To accomplish this increase in energy, the liquid must absorb heat. The number of calories of heat that must be absorbed by a specific amount of liquid in order to increase its temperature 1°C is referred to as the *specific heat.* The specific amount of liquid

is either 1 g or 1 mole, specific heat being therefore expressed in units of calories per gram or calories per mole. The absorption of heat by a liquid when its temperature is raised and, vice versa, the giving off of heat when the liquid cools, are the bases for its use as a cooling agent or warming agent. Water has the highest specific heat of any substance. That fact, plus its availability and cheapness, makes it a widely used cooling agent in car radiators and industrial cooling systems and a heating medium in hot-water bottles and hot-water heating systems.

2.19 Freezing of a liquid. As the temperature of a liquid decreases, the energy of its moving molecules decreases. Finally, the molecules of lowest energy are pulled together by the intermolecular forces into a rigid, oriented, patterned, solid crystal structure. The process is called *freezing, crystallization,* or *solidification,* and the definite temperature at which it occurs is called the *freezing point* of the liquid. Because the molecules are at a lower energy level in the definitely oriented solid state than in the liquid state, heat energy is given off when a substance freezes; this is called *heat of crystallization* and is expressed in units of calories per gram or calories per mole. At the freezing point the solid and liquid molecules are in equilibrium. As a result, the temperature remains constant during the freezing process. Every pure liquid substance has a definite freezing point; the definiteness of this freezing temperature makes it a convenient means of identifying the liquid.

2.20 Properties of solids. The solid that is formed when a liquid element or compound freezes has the following characteristic properties.

A. *Definite, Characteristic Crystal Structure.* Every true solid exists as a crystal of definite form in which the molecules or ions are fitted together in a definite geometrical pattern. The exact crystal form which a specific solid takes is determined by the structure and shape of the ions or molecules of the substance and the disposition of the attractive forces which bind them together (see Figures 2.9 and 2.10). Because a given molecule has a definite shape and structure and because the forces which cause it to be attracted by other molecules are definitely

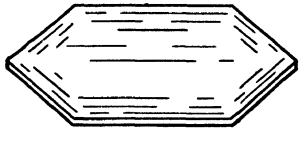


Figure 2.9. Flat hexagonal naphthalene crystal.

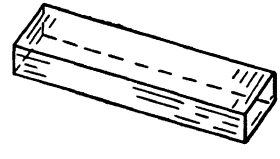


Figure 2.10. Rectangular crystal of sodium thiosulfate.

ordered, these molecules will always crystallize in the same pattern. The number of these definite crystal patterns runs into the thousands; the expert crystallographer can, however, place every crystal pattern, however complex, in one of six basic crystallographic systems.

B. *Definite X-Ray Pattern.* Because every true solid is built up according to a definite geometrical pattern to form a crystal of definite structure, this crystal will reflect x-ray waves in a definite manner. This gives rise to a definite pattern of reflected waves. An analysis of this x-ray pattern enables the expert to predict the manner in which the molecules are arranged in the crystal.

C. *Definite Melting Point.* It was pointed out in Section 2.19 that at its freezing point, a liquid exists in equilibrium with its crystalline solid and that as a result, the temperature remains constant, while the liquid is transformed into a solid. It follows therefore that when a solid is heated, it will change to a liquid at the same constant temperature at which it was originally formed from the liquid, and during this transformation the solid will be in equilibrium with the liquid. The temperature at which the solid changes to a liquid is called the *melting point.* Just as heat is evolved when a liquid freezes, so is an exactly equivalent amount of heat absorbed when the solid melts. This is called *heat of fusion* and is expressed in units of calories per gram or calories per mole. The heat of fusion of ice is 79.9 cal per gram.

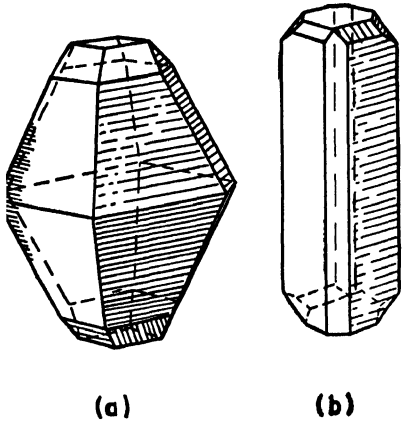


Figure 2.11. Allotropic forms of sulfur: (a) rhombic; (b) monoclinic.

Because every pure solid substance has a definite melting point which is practically unaffected by change of pressure, the determination of this melting point is one of the most widely used methods for aiding in the identification of solids. The melting points of hundreds of solid substances are listed in tables such as the *International Critical Tables.*

2.21 Allotropic forms. Many substances can exist in more than one definite crystalline form. These different crystalline forms are referred to as *allotropic forms* or *allotropes.* The change from one crystal form to another takes place at a definite constant temperature in an equilibrium process and is attended by absorption or evolution of a

definite amount of heat called the *heat of transition.* The temperature at which the change takes place is called the *transition temperature.* Sulfur exists as rhombic crystals at temperatures below 95.5°C. When heated it changes to needle-shaped monoclinic crystals at 95.5°C, the temperature remaining constant during the equilibrium transition. When monoclinic sulfur is cooled it changes to the rhombic form at 95.5°C (see Figure 2.11). Carbon occurs in one crystalline form in graphite and another form in diamond.

2.22 Sublimation. Most stable solids, when heated in an open vessel, melt equilibrium-wise at a definite temperature to form a liquid. At some higher definite temperature the liquid boils, equilibrium-wise, to yield a vapor.

Some solids, however, change directly to a vapor without first melting, and the resulting vapor in turn changes back to a solid without first condensing to a liquid. Furthermore, the solid to vapor transformation is an equilibrium process and, at a definite pressure, takes place at a definite constant temperature. This equilibrium-wise transformation of a solid to a vapor is called *sublimation,* and the amount of heat required to accomplish this change is called *heat of sublimation.*

Just as molecules of all liquids tend to escape (evaporate) into the open air from the surface of the liquid, so molecules of all solids tend to escape directly into the atmosphere from the surface of the solid. Just as the vapor pressure, that is the tendency of liquid molecules to escape, increases with increase in temperature, so does the vapor pressure of a solid increase with increase in temperature. Just as a liquid will boil when its vapor pressure equals the pressure of the atmosphere, so a solid will sublime when its vapor pressure equals the pressure of the atmosphere. Most solids have such low vapor pressures that they melt before the temperatures at which their vapor pressure equals the atmospheric pressure is reached; as a result they do not have a chance to sublime. A few solids, such as iodine and ammonium chloride, have vapor pressures so high that they equal the atmospheric pressure at temperatures below the melting point of the solid; these solids will sublime rather than melt.

Since a solid will sublime when its vapor pressure equals the outside pressure, it follows that if the outside pressure is increased the sublimation temperature will be increased. If the outside pressure is high enough the solid will melt before its vapor pressure gets high enough to cause it to sublime. The melting point of a solid which sublimes at ordinary atmospheric pressure can thus be determined by heating it under pressure. Conversely, a solid which normally melts can be made

to sublime by heating it under reduced pressure. This latter technique has important industrial application in the purification of substances by sublimation. The high vapor pressures of solids like naphthalene (moth balls), camphor, and paradichlorobenzene are indicated by the strong odors which they evolve. The fact that ice and snow will slowly disappear even during below-freezing temperatures shows that solid H_2O has an appreciable vapor pressure.

Questions and Problems

1. Define or describe and illustrate each of the following: gas; liquid; solid; fluid; kinetic energy; kinetic theory; pressure; standard pressure; barometric pressure; atmospheric pressure; 1 atm of pressure; standard temperature; absolute temperature; absolute zero; diffusion; Boyle's law; Charles's law; molar volume; Avogadro's hypothesis; Avogadro number; gas density; partial pressure; mol fraction; Dalton's law of partial pressures; Graham's law of diffusion; liquefaction; condensation of a gas; critical temperature; critical pressure; vapor pressure; equilibrium; principle of Le Chatelier.

2. How does the kinetic-molecular theory account for the following facts?

(a) A gas expands indefinitely.

(b) A gas exerts pressure.

(c) The volume of a mass of gas is inversely proportional to the pressure.

(d) The volume of a mass of gas is directly proportional to the absolute temperature.

(e) The pressure exerted by a gas is inversely proportional to the volume.

3. You are given a sample of SO_2 gas at 180°C and 750 mm. Describe how you would liquefy it.

4. Define or describe and illustrate each of the following: boiling; boiling point; volatile liquid; heat of vaporization; heat of condensation; distillation; evaporation; relative humidity; dew point; specific heat; freezing; freezing point; crystal; melting point; heat of fusion; allotropic forms; transition temperature; heat of transition; sublimation.

5. Point out how the principle of Le Chatelier operates when a 100 ml flask containing 10 ml of water is slowly evacuated.

6. A large cylinder fitted with a frictionless piston contains 32.3 l of steam at 120°C. The total pressure on the steam (the atmospheric pressure plus the weight of the piston) is equal to 760 mm of mercury.

A current of cold air is blown at the assembly in such a manner and at such a rate that the cylinder and its contents are cooled very slowly. The final temperature of the assembly is −2°C. Assuming that the H_2O exists as molecules and you are able to see them, describe in detail exactly what you would observe during the entire cooling process.

7. Explain each of the following:

(a) When a warm current of air falls upon skin that is wet with warm water a sensation of cold results.

(b) The operation of the cooling unit in a refrigerator.

(c) Tubs of water, set in storage cellars, will keep stored produce from freezing.

(d) At a given pressure a pure liquid boils at a constant temperature.

(e) The temperature of ice water stays at 0°C as long as there is ice in the water.

(f) Drinking water can be kept cool on a warm day by placing it in a semiporous canvas bag and hanging it in the wind.

(g) When the nozzle of a fire extinguisher tank containing liquefied CO_2 at room temperature is kept open for a while, a spray of CO_2 "snow" is formed.

(h) Steam at 100°C will produce a more severe burn than hot water at 100°C.

(i) Wet towels dry faster on warm, dry, windy days than on sultry, humid, windless days.

(j) Water boils at a lower temperature on top of a mountain than at sea level.

(k) At the start of a trip the air pressure in an automobile tire was 28 lb; at the middle of the trip two hours later measurement with the same gage showed a pressure of 30 lb.

8. The volume of a dry gas is 400 ml at 0°C and 760 mm. What volume will it occupy at 0°C and 732 mm?

9. The volume of a dry gas is 600 ml at 12°C and 740 mm. What volume will it occupy at 0°C and 740 mm?

10. The volume of a dry gas is 800 ml at 40°C and 742 mm. What volume will it occupy at standard conditions?

11. The volume of a dry gas is 500 ml at 30°C and 750 mm. What volume would it occupy if collected over water (in which it is insoluble) at 746 mm and 40°C? The vapor pressure of water at 40°C is 55 mm.

12. What volume will 50 g of the gas C_2H_6 occupy at STP?

13. What volume will 100 g of CH_4 gas occupy at 20°C and 740 mm?

14. Calculate the weight in grams of 100 l of CO_2 gas at STP; of 200 l of H_2S gas measured at 25°C and 730 mm?

15. What volume will 2 moles of SO_2 gas occupy at STP?

16. (a) Derive the formula for Graham's law from the kinetic energy equation, KE = $\frac{1}{2}mv^2$.

(b) Derive the combined gas law formula.

(c) Derive the general gas law equation, $PV = nRT$.

17. Show that the following statements are true:

(a) The weight of equal volumes of gases at the same temperature and pressure are to each other as the molecular weights of the gases.

(b) The densities of two gases, at the same temperature and pressure, are to each other as their molecular weights.

18. A mixture of 10 g of CH_4 gas and 10 g of CO_2 gas is placed in a container under a pressure of 760 mm of mercury. Calculate the partial pressure of the CH_4 gas in the mixture.

19. Methane gas diffuses through a porous disk at the rate of 28 cc per minute. How fast will HCl gas diffuse through the same disk at the same temperature and pressure?

20. Calculate the density of NO_2 gas in grams per liter at 25°C and 740 mm.

21. One hundred liters of a dry, gaseous compound measured at 27°C and 745 mm weighed 90.0 g. Calculate its approximate molecular weight.

22. A gaseous compound contains 92.3% carbon and 7.7% hydrogen, and 41.8 g of the dry gas occupied a volume of 13.6 l at 20°C and 720 mm. Calculate the true chemical formula of the compound.

CHAPTER 3

Oxygen

Up to this point we have learned something about the general characteristics of elements and compounds and the properties of the gaseous, liquid, and solid states in which these elements and compounds exist. We will next make a detailed study of the two elements oxygen and hydrogen. Not only will this study give us a lot of specific information about oxygen and hydrogen and their compounds, but it will introduce us to all the elements and compounds with which they react. As a result we will gain enough acquaintance with the elements so that we will be able to consider intelligently, in Chapters 6, 7, and 8, their orderly arrangement and grouping in the periodic table and the detailed structure of the atoms of each element. With the generalizations that can be drawn from the periodic table and the structure and sizes of each of the atoms as guides, we will be able to examine the behavior of the remaining elements and compounds with a maximum of logical reasoning and a minimum of rote memory.

3.1 Importance of oxygen. Oxygen is in a sense the most important element, being absolutely essential to the existence of practically all animal and plant life.

It is the most plentiful element in the world. Free oxygen gas makes up about 21% by volume of the air that we breathe. About 65% of the weight of the human body is oxygen, all of it in the form of compounds such as water, proteins, and fats. It is one of the main constituents of all forms of plant and animal life. In the form of hundreds of compounds it makes up 49.2% of the weight of the earth's crust. Some of the more important and abundant oxygen compounds in nature are water (H_2O), sand (SiO_2), limestone ($CaCO_3$), clay ($HAlSiO_4$), feldspar ($KAlSi_3O_8$), hematite iron ore (Fe_2O_3), gypsum ($CaSO_4 \cdot 2H_2O$), starch ($C_6H_{10}O_5$), and sugar ($C_{12}H_{22}O_{11}$).

Oxygen will, we shall learn, combine with nearly every other element. It thus provides an excellent means of introduction to these elements.

3.2 Identification of oxygen. The study of every element and compound generally resolves itself into finding the answers to such

questions as, How can it be identified? What are its important physical properties? With what other elements and compounds does it react? How can it be prepared in the laboratory? How is it prepared commercially? What is it used for? What important principles does its behavior illustrate?

Oxygen is a colorless, odorless, and tasteless gas. Obviously then it cannot be identified by sight or smell. A glowing wood splint will burst into bright flame when thrust into oxygen gas, and a burning splint will flare up brightly. This provides a simple and decisive means of identification. The reaction that takes place in the test will be discussed later.

3.3 Physical properties of oxygen. The fact that oxygen is a colorless, odorless, and tasteless gas has already been mentioned. The formula of its gaseous molecule is O_2; it has a density of 32 g/22.4 l at STP. It has a critical temperature of − 118.8°C and a critical pressure of 49.7 atm; that means that air must be cooled below −118.8°C before the oxygen present can be liquefied. At a pressure of 760 mm liquid oxygen boils at −183°C.

Oxygen gas is only slightly soluble in water. That means that it can be collected in the laboratory by displacement of water and can be stored over water.

3.4 Chemical properties of oxygen. Attention was called in Chapter 1 to the fact that when the metal magnesium is heated in the presence of oxygen gas it takes fire and burns brilliantly, a large amount of heat being given off and a white solid compound, magnesium oxide (MgO), being formed as the product of the reaction. This reaction illustrates the behavior of oxygen toward most elements. It is a very reactive element. Under the proper conditions of temperature and pressure, it will react with every element except the gases helium, neon, argon, krypton, xenon, and radon, and the metals gold and platinum. An oxide of the element is formed in every case. As in the burning of magnesium, heat may be necessary to make the reaction go rapidly, the required temperature being in some instances quite low, and in others extremely high. In most instances, once the reaction is started, it proceeds spontaneously with evolution of heat; that is, it is *exothermic*. In a few cases the reaction is *endothermic*, and continued application of heat is necessary to keep it going.

Oxygen also reacts with hundreds of different compounds. The burning of wood (cellulose, $C_6H_{10}O_5$) and of natural gas (methane, CH_4) are typical examples. Here again heat is necessary to initiate the reac-

tion, which generally is exothermic but in a few cases is endothermic. In the majority of cases the oxides of the elements of which the compound is composed are formed as products.

A. *Reactions of Oxygen with Metals. Balancing Chemical Equations.* The reaction that takes place when oxygen combines with metallic magnesium can be represented by the following *word equation:*

$$\text{magnesium} + \text{oxygen} = \text{magnesium oxide} + \text{heat (evolved)}$$

The empirical formula for magnesium oxide has been determined, in the manner already discussed in Chapter 1, to be MgO. The formula for oxygen gas is O_2. The formula for magnesium is Mg. If we substitute these formulas for the names in the word equation we obtain the following *skeleton equation:*

$$Mg + O_2 = MgO + \text{heat}$$

There evidently is something incorrect about this equation, because 1 mole of MgO containing only *1* gram-atom of oxygen is being formed from 1 mole of oxygen which contains *2* gram-atoms of oxygen. If we start with 2 gram-atoms (1 mole) of oxygen we must end with 2 gram-atoms. If 1 gram-atom of oxygen combines with 1 gram-atom of magnesium to form 1 mole of MgO, then the 2 gram-atoms of oxygen in 1 mole of O_2 will combine with 2 gram-atoms of magnesium to form 2 moles of MgO. The correct equation will then be

$$2\,Mg + O_2 = 2\,MgO + \text{heat}$$

This is a *balanced chemical equation.* That it is *balanced* is shown by the fact that the number of gram-atoms of magnesium and of oxygen on the right-hand side of the equation is the same as the number on the left. *In any balanced chemical equation the number of gram-atoms of each element on the left must be the same as the number on the right.*

One might argue that the skeleton equation could have been balanced correctly by changing the formula of MgO to MgO_2. The equation would then have been

$$Mg + O_2 = MgO_2 + \text{heat}$$

The equation *is* balanced but it *is not correct.* The formula for magnesium oxide is not MgO_2; it is MgO.

Likewise it might be argued that the skeleton equation could have been balanced by changing the formula of oxygen gas to O. The equation would then have been

$$Mg + O = MgO + \text{heat}$$

This equation is balanced but it is not correct. Oxygen gas is not monatomic; its molecule is diatomic and its formula is O_2. First and foremost, *a chemical equation must represent correctly the experimental facts.* That means that all formulas must represent correctly the true composition of all reactants and products. If the formula of a substance is wrong the equation is incorrect even if it is balanced.

Summarizing what has been stated, writing a balanced equation for a chemical reaction involves the following steps:

1. *Write the word equation,* giving the names of the reactants and products. As one becomes well grounded in chemical information the actual *writing* of the word equation can be omitted; the *thinking* of this word equation must always be the first step in writing the balanced chemical equation.

2. *Write the correct formulas for all reactants and products.* Once the *correct* formulas have been written they must not be changed in the balancing process.

3. *Balance the equation.* This is done by taking the smallest numbers of moles of reactants and products that are necessary to give the same number of gram-atoms of each element, respectively, on both sides of the equation.

The above steps can be illustrated by writing the balanced equation for the reaction that takes place when the metal calcium is heated in an atmosphere of oxygen gas.

Writing the word equation. How can we know whether or not a reaction takes place when calcium is heated in the presence of oxygen and how can we know what product is formed? Actually the only way to know is to carry out a series of experiments. Every fact, every bit of information, every equation in this book and every other textbook, are the results of experimentation. Chemists have heated every metal in the presence of oxygen and have found that every single one except gold and platinum reacts with it. The results of their experimentation are summarized in the conclusion that every metal except gold and platinum will combine with oxygen to form the oxide of the metal. This conclusion can be expressed in the form of a simple word equation:

$$\text{metal} + \text{oxygen} = \text{metal oxide}$$

We can verify this conclusion if we have the necessary analytical experience or, as most generally happens in the average beginning chemistry course, we can accept it without attempt at verification. In either case we can write the word equation.

$$\text{calcium} + \text{oxygen} = \text{calcium oxide}$$

Writing the correct formulas for all reactants and products. Here again we must either do our own experimentation or rely upon the experimental evidence that has been obtained by hundreds of scientists. In view of the mass of chemical facts the latter becomes the practical alternative; we find, on the basis of such evidence, that the formulas of calcium, oxygen, and calcium oxide are, respectively, Ca, O_2, and CaO. Instead of memorizing, as a specific fact, that the formula for a molecule (or, what amounts to the same thing, the symbol for an atom) of calcium is Ca it is simpler and more efficient to remember that *all metals, being either solids or liquids at room temperature, form monatomic molecules.* Therefore calcium, being a metal, has the formula Ca. Likewise, we could memorize the formula for oxygen gas as a specific fact. It will be more efficient to place it in a group with the other reactive elemental gases (H_2, N_2, F_2, Cl_2, Br_2, and I_2) and recall that they all form diatomic molecules. The monatomic gases are helium, neon, argon, krypton, xenon, and radon. These six gases do not react with oxygen; as a matter of experimental fact they do not react with any element no matter how high the temperature and pressure, and are therefore considered to be chemically inert. If an element which is a gas at room temperature does react, its molecule is diatomic; the only monatomic elemental gases are the inert ones.

Because there are thousands of different compounds, recalling the correct formula of each one is more of a problem. We can either (a) memorize or look up each specific formula, which is what generally is done at the outset, or (b) we can memorize a key formula or reference formula for each element or radical and use it as a means of remembering the valence of the element, and hence as a guide in writing the formulas of other compounds, or (c) we can memorize the valences of the common elements and radicals listed in Table 1.4 and from these valences deduce the formula of the new compound. Thus if we know that the formula for calcium chloride is $CaCl_2$ and that for water is H_2O, or if we have memorized the facts of Table 1.4 and know that calcium and oxygen each have a valence of 2, we can readily deduce that the simple formula of calcium oxide is CaO. Deduction of one formula from another or from a table of valences assumes that an element or radical will always have the same valence. This assumption is true for all the radicals (sulfate, SO_4; nitrate, NO_3; etc.) and for most of the common metals that will be encountered in the early part of this course. The fact that a majority of the elements do display different combining capacities (valences) under different circumstances will obviously complicate this method of deducing formulas. Fortunately, these variable valences do

not show up in our study until we get beyond Chapter 15; by then they will be relatively easy to cope with.

In concluding this section it should be re-emphasized that the formula for every compound and the equation for every reaction have been derived from carefully conducted laboratory experiments. No chemist preparing new compounds and carrying out new reactions will ever determine the formula of a new compound from the formulas of related compounds and let it go at that; he always seeks to deduce the formula from the data that he gets in the laboratory.

Balancing the equation. Having decided that the skeleton equation is

$$Ca + O_2 = CaO$$

it now is a simple matter to observe that 2 gram-atoms of calcium will combine with the 2 gram-atoms of oxygen in 1 mole of O_2 to form 2 moles of CaO. The balanced equation then becomes

$$2\,Ca + O_2 = 2\,CaO$$

The third of the above steps, balancing an equation, is quickly and easily mastered and gives few students any trouble. With a little effort in memorizing a few formulas and valences and a little thought in the use of this memorized information, the second step, writing the correct formulas of reactants and products, is relatively simple and causes the average student no difficulty. The real problem in chemistry is to know what happens when two reacting substances are brought together, and thus to be able to write, or think, the correct word equations. Once we have the correct word equation the rest is easy.

The formulas for the oxides of all divalent metals will correspond to those for magnesium and calcium oxides. Thus we have the more common oxides ZnO, CuO, FeO, PbO, and HgO and the less familiar oxides BeO, SrO, BaO, RaO, CdO, CoO, NiO, and SnO.

The balanced equation for the reaction of oxygen with a monovalent metal, such as sodium, is

$$4\,Na + O_2 = 2\,Na_2O$$

and with a trivalent metal such as aluminum is

$$4\,Al + 3\,O_2 = 2\,Al_2O_3$$

In balancing this latter equation we find, on examining the skeleton equation

$$Al + O_2 = Al_2O_3$$

that, whereas in oxygen gas the oxygen exists in units of two atoms, in Al_2O_3 it is present in units of three atoms. The least common multiple

of 2 and 3 is 6. Therefore, a total of 6 gram-atoms or 3 moles of oxygen must react, and these 3 moles of oxygen will produce 2 moles of Al_2O_3. This, however, will require 4 gram-atoms of aluminum. The balanced equation will therefore be

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

The formulas for the oxides of all monovalent metals will be the same as for Na_2O, and the equations for the reactions of these metals with oxygen will be the same as that for sodium. Thus we have the simple formulas Li_2O, K_2O, Rb_2O, Cs_2O, and Ag_2O, and the equation

$$4\ Ag + O_2 = 2\ Ag_2O$$

The formulas for the oxides of all trivalent metals will be the same as that for aluminum. Accordingly, we have Fe_2O_3, Cr_2O_3, and Bi_2O_3, and

$$4\ Cr + 3\ O_2 = 2\ Cr_2O_3$$

What a chemical equation represents. Having considered how to balance an equation we can reflect for a moment on just what the resulting equation represents. The balanced equation is a form of chemical shorthand. Thus the equation

$$2\ Mg + O_2 = 2\ MgO$$

states simply that magnesium reacts with oxygen in the *ratio* of 2 gram-atoms of magnesium to 1 mole of oxygen, and that the MgO is formed in the ratio of 2 gram-formula weights of MgO to 2 gram-atoms of magnesium and 1 mole of oxygen. Whether we burn a pinch of magnesium or a barrelful, the weight of the MgO formed will be to the weight of magnesium burned as the weight of 2 gram-formula weights of MgO is to the weight of 2 gram-atomic weights of magnesium. Just how the equation can be used in the solution of problems will be discussed in Chapter 5.

B. *Reaction of Oxygen with Nonmetals.* The following word and balanced chemical equations illustrate the reaction of oxygen with typical nonmetals.

1. Carbon + oxygen = carbon dioxide (gas)
   $C + O_2 = CO_2 + \text{heat}$
2. Sulfur + oxygen = sulfur dioxide (gas)
   $S + O_2 = SO_2 + \text{heat}$
3. Silicon + oxygen = silicon dioxide (solid)
   $Si + O_2 = SiO_2 + \text{heat}$

4. Nitrogen + oxygen = nitrogen monoxide (gas)
$$N_2 + O_2 + \text{heat} = 2\,NO$$

5. Hydrogen + oxygen = water (liquid)
$$2\,H_2 + O_2 = 2\,H_2O + \text{heat}$$

6. Phosphorus + oxygen = phosphorus oxide (solid)
$$4\,P + 5\,O_2 = P_4O_{10} + \text{heat}$$

As in the case of the reactions of oxygen with metals, heat is necessary to start the reaction, the required temperature running as high as 2000°C in the reaction with nitrogen. Most of the reactions are exothermic; a few, such as the reaction with nitrogen, are endothermic.

C. *Reaction of Oxygen with Compounds.* Because oxygen reacts with such a large number of compounds, and because this number includes so many different types of substances, it would be confusing at this stage to try to present a complete discussion of this aspect of the chemical behavior of oxygen. Therefore its reaction with only a few common compounds will be considered.

1. *Burning of methane gas,* CH_4:

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O + \text{heat}$$

Methane is the chief component of natural gas. Therefore this reaction is of tremendous importance as a source of heat in household furnaces and gas stoves, in industrial power plants, and in commercial manufacturing installations.

It should be noted that most compounds which contain the element carbon (CH_4, C_2H_5OH, $C_6H_{10}O_5$, etc.) are referred to as *organic* compounds; they are so called because all living (organic) substances contain carbon compounds. The study of the chemical behavior of carbon and its compounds is called *organic chemistry.* In contrast, the study of the noncarbon-containing compounds and the elements that make up these compounds is referred to as *inorganic chemistry.* These two branches of chemistry overlap a great deal.

2. *Burning of wood cellulose,* $C_6H_{10}O_5$: This is the reaction that takes place when oxygen gas is identified by testing with a glowing splint.

$$C_6H_{10}O_5 + 6\,O_2 = 6\,CO_2 + 5\,H_2O$$

3. *Burning of ethyl alcohol,* C_2H_5OH:

$$C_2H_5OH + 3\,O_2 = 2\,CO_2 + 3\,H_2O$$

4. *Burning of carbon disulfide,* CS_2:

$$CS_2 + 3\,O_2 = CO_2 + 2\,SO_2$$

5. *Burning of octane,* C_8H_{18}: Octane is one of the components of gasoline.

$$2\ C_8H_{18} + 25\ O_2 = 16\ CO_2 + 18\ H_2O$$

The balancing of this equation can be done by a systematic method of trial and error as follows: First write the skeleton equation,

$$C_8H_{18} + O_2 = CO_2 + H_2O$$

One mole of C_8H_{18} contains enough carbon and hydrogen to yield 8 moles of CO_2 and 9 moles of H_2O. We will then have, as a first trial,

$$C_8H_{18} + ?\ O_2 = 8\ CO_2 + 9\ H_2O$$

This will call for 25 gram-atoms or $12\frac{1}{2}$ moles of oxygen. But since we prefer not to deal with $\frac{1}{2}$ mole of oxygen, and hence an odd number of gram-atoms of oxygen gas, we must take 2 moles of C_8H_{18}. This will yield 16 moles of CO_2 and 18 moles of H_2O and will require 50 gram-atoms, or 25 moles, of oxygen. The balanced equation will then be as given above.

6. *Burning of lead tetraethyl,* $Pb(C_2H_5)_4$: This compound is the anti-knock component in "ethyl" gasoline. Like the preceding equation, this can be balanced by trial and error.

$$2\ Pb(C_2H_5)_4 + 27\ O_2 = 2\ PbO + 16\ CO_2 + 20\ H_2O$$

7. *Roasting of a metal sulfide ore:*

$$2\ PbS + 3\ O_2 = 2\ PbO = 2\ SO_2$$

This reaction represents the first step in the recovery of lead from its ore, galena (PbS).

It will be noted that in each of the above reactions the products are the oxides of the elements of which the compound is composed. This is generally true of all reactions in which a compound is burned in air or oxygen. There are, however, numerous reactions in which more complex compounds rather than oxides of the constituent elements are formed. Several such reactions will be encountered later in this book. At the present time only those reactions that yield oxide products need be considered. One can then state, as a general rule that *if a compound burns in air or oxygen the products will be the oxides that would be formed if the constituent elements, independently, were burned in oxygen.* Thus zinc ethyl, $Zn(C_2H_5)_2$, which burns readily in oxygen or air, will yield ZnO, CO_2, and H_2O as products.

3.5 Oxidation. In each reaction in which an element combines with oxygen the oxide is formed as a product. For that reason such reactions

have long been referred to as *oxidation reactions.* The process by which the element is converted to its oxide is referred to as *oxidation,* and the element with which the oxygen reacts is said to be *oxidized.* Since the oxygen causes the element to be oxidized it is said to be the *oxidizing agent.* Thus the reaction represented by the equation

$$2\,Cu + O_2 = 2\,CuO$$

illustrates oxidation. Copper is oxidized to CuO and oxygen is the oxidizing agent.

3.6 Oxidation state. Oxidation number. Since magnesium is said to be oxidized to MgO in the reaction

$$2\,Mg + O_2 = 2\,MgO$$

it is correct to say that the magnesium in MgO is in a *higher state of oxidation* than it is in metallic magnesium. The evidence to support this statement is the concept that the valence of metallic magnesium is 0, while its valence in MgO is 2. Using these *valence numbers* as the basis for determining the state of oxidation, we can then say that when magnesium is oxidized to MgO its *oxidation state* or *oxidation number* is increased from 0 to 2. What has been said about magnesium will apply to every element with which oxygen reacts, the differences being only in the actual values of the oxidation numbers.

As a standard of reference to use in determining the oxidation number of an element, hydrogen in its compounds is arbitrarily assigned an oxidation number of $+1$. Since 1 atom of oxygen combines with 2 atoms of hydrogen, the oxidation number of oxygen in its compounds is -2; the sign is negative to show that, since it combines with hydrogen, its polarity is opposite to that of hydrogen. *A free element is assigned an oxidation number of 0.* The oxidation number of an element in a binary compound is determined by reference to the hydrogen or oxygen (or their equivalent) with which it is combined. Thus the oxidation number of C in CH_4 is -4, of Zn in ZnO is $+2$, of Cl in HCl is -1, of Al in Al_2O_3 is $+3$, of P in P_4O_{10} is $+5$, of S in H_2S is -2, of C in CO_2 is $+4$, and of S in SO_2 is $+4$. If the binary compound does not contain either oxygen or hydrogen, the oxidation numbers are determined by indirect reference to one of these elements. Thus because ZnS is analogous to H_2S in which the oxidation number of S is -2, we can reason that the oxidation number of S is -2; Zn will then have an oxidation number of $+2$. Because Cl has an oxidation number of -1 in HCl we can reason that it has the same oxidation number in the binary compound, $SnCl_4$. The oxidation number of Sn in $SnCl_4$ is therefore $+4$. Metals always

have positive oxidation numbers in their binary compounds; therefore in these compounds the nonmetal will have a negative oxidation number.

The oxidation number of an element in its ternary compound is determined by applying the rule that in any compound the sum of the positive oxidation numbers must equal the sum of the negative oxidation numbers. Thus in the compound H_2SO_4 the oxidation number of S can be determined to be +6 as follows: The 2 atoms of H will have a total oxidation number of +2 and the 4 atoms of oxygen will have a total oxidation number of −8. Therefore, to equalize the positive and negative values, S must have an oxidation number of +6. In a similar manner the oxidation number of N in HNO_3 can be calculated to be +5, of P in H_3PO_4 is +5, of each chromium atom in $H_2Cr_2O_7$ is +6, and of each boron atom in $H_2B_4O_7$ is +3. In ternary compounds containing metals, such as Na_2SO_3, the oxidation number of the metal is first deduced by reference to the related hydrogen compound. In the above instance the related compound is H_2SO_3. Since the oxidation number of each of the 2 hydrogens in H_2SO_3 is +1 and since the 2 atoms of sodium have obviously taken the place of 2 atoms of hydrogen, the oxidation number of each atom of sodium must be +1. The 3 atoms of oxygen have a total oxidation number of −6. Therefore the oxidation number of S in Na_2SO_3 is +4.

Oxidation number refers only to the state of oxidation of an *element*. One does not, therefore, speak of the oxidation number of a radical. A radical has valence but not an oxidation number. Thus in the compound H_2SO_4, the SO_4 radical has a valence of 2, and the sulfur in the radical has an oxidation number of +6.

3.7 Oxidation number and oxidation. As has already been stated, when an element is oxidized its oxidation number is increased. It follows therefore that if the oxidation number of an element is increased the element is oxidized. One can therefore define *oxidation* as a *reaction process in which the oxidation number of an element is increased.*

3.8 Oxidation in the absence of oxygen. Magnesium will burn in an atmosphere of chlorine gas just about as briskly as it does in oxygen. The product is the solid compound magnesium chloride, $MgCl_2$. The equation for this reaction is

$$Mg + Cl_2 = MgCl_2 + \text{heat}$$

In this reaction the oxidation number of magnesium is increased from 0 in Mg to +2 in $MgCl_2$. (The oxidation number of chlorine, deduced

from the compound HCl, is -1.) Magnesium has been oxidized, and chlorine is the oxidizing agent.

Magnesium reacts with fluorine gas even more vigorously than it reacts with either chlorine or oxygen. The equation for the reaction is

$$Mg + F_2 = MgF_2 + \text{heat}$$

In this reaction the magnesium is oxidized, because its oxidation number is increased from 0 in Mg to $+2$ in MgF_2. (The oxidation number of fluorine, deduced from the compound HF, is -1.) Fluorine is the oxidizing agent; the vigor of its reaction with magnesium indicates that it is a more powerful oxidizing agent than either oxygen or chlorine.

Magnesium will react with the nonmetals Br_2, I_2, N_2, S, P, Si, Se, and Te according to the following equations.

$Mg + Br_2 = MgBr_2$ (magnesium bromide)
$Mg + I_2 = MgI_2$ (magnesium iodide)
$3\,Mg + N_2 = Mg_3N_2$ (magnesium nitride)
$Mg + S = MgS$ (magnesium sulfide)
$3\,Mg + 2\,P = Mg_3P_2$ (magnesium phosphide)
$2\,Mg + Si = Mg_2Si$ (magnesium silicide)
$Mg + Se = MgSe$ (magnesium selenide)
$Mg + Te = MgTe$ (magnesium telluride)

In each of these reactions the oxidation number of magnesium is increased from 0 to $+2$; therefore it is oxidized. The element with which it reacts is in each case the oxidizing agent. It is obvious from the examples that have been cited that *nonmetals as a class tend to function as oxidizing agents.*

There is considerable difference in the vigor with which each of the above oxidizing agents reacts with magnesium. Bromine is less reactive than chlorine but is more reactive than iodine, while silicon is the least reactive of those considered. We thus see that different oxidizing agents differ markedly in their oxidizing power.

With some exceptions all metals behave like magnesium. They all have their oxidation numbers increased from 0 to some definite positive value when they react with the nonmetals included in the preceding equations. Therefore they are all oxidized, and the nonmetals with which they react act as oxidizing agents.

The term *oxidation* refers, therefore, to any reaction process in which the oxidation number of an element is increased, regardless of whether or not oxygen is involved. When the oxidation number of an element is increased, by any substance or process, that element is said to be *oxidized.* Any substance that will react in such a way that it

causes the oxidation number of an element to be increased is an *oxidizing agent.*

3.9 Elements with several oxidation numbers. When carbon is burned in oxygen or air, carbon dioxide is formed according to the reaction

$$C + O_2 = CO_2$$

If the oxidation of carbon by oxygen is carried out at a temperature of around 1000°C in the presence of a limited supply of oxygen, carbon monoxide is formed according to the reaction

$$2\,C + O_2 = 2\,CO$$

Carbon monoxide will burn in air to form CO_2.

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

In CO, carbon has an oxidation number of +2, while in CO_2 it has an oxidation number of +4. Carbon takes the lower oxidation number when the oxidizing conditions are unfavorable (limited supply of oxygen) and the higher number when the oxidizing conditions are more favorable (plentiful supply of oxygen).

Likewise tin may form SnO or SnO_2 depending on conditions, copper forms CuO and Cu_2O, iron forms FeO and Fe_2O_3, sulfur will yield SO_2 or SO_3, phosphorus forms P_2O_3 and P_4O_{10}, iron forms $FeCl_2$ and $FeCl_3$, tin forms SnS and SnS_2, phosphorus forms PCl_3 and PCl_5, while nitrogen may exist as N_2O, NO, N_2O_3, NO_2, N_2O_5, N_2H_4, and NH_3, in which compounds its oxidation numbers are, respectively, +1, +2, +3, +4, +5, −2, and −3. Similar examples might be cited for other elements, all pointing to the fact that the oxidation number of an element may vary with the conditions under which the compound is formed. There is nothing surprising about this fact; it simply means that the capacity of an element for combining with other elements may vary with the conditions that prevail when it combines. We shall find, as we proceed with our study, that the conditions that determine the oxidation state that an element will take are fairly well defined and easy to interpret. It is customary, in writing the name of the compound of a multiple-oxidation-state element to designate its oxidation number in this particular compound by a Roman numeral. Thus we speak of iron(III) chloride and mercury(II) oxide.

Law of multiple proportions. The fact that carbon forms CO and CO_2, that sulfur forms SO_2 and SO_3, that iron forms $FeCl_2$ and $FeCl_3$, and that copper forms CuO and Cu_2O is in no way contrary to the law of definite composition. Carbon monoxide and CO_2 are each definite

and distinctly different chemical compounds, and the composition of each is constant and definite. The same is true of the others listed.

It will be noted that the compositions of the two different compounds of each pair of elements listed differ by small whole-number units. This fact, which is in accord with the atomic theory which postulates that molecules of compounds are formed by the combination of specific small numbers of atoms of two or more elements, is expressed by the law of multiple proportions; it states, in principle, that *when different weights of element B* (oxygen, in the case of CO and CO_2) *combine with a fixed weight of A* (carbon in CO and CO_2) *the different weights of B are in the ratio of small whole numbers* (1 to 2 in CO and CO_2, 2 to 3 in $FeCl_2$ and $FeCl_3$, 2 to 3 in FeO and F_2O_3).

3.10 Combustion. Kindling temperature. When a reaction proceeds at such speed and with evolution of so much heat and light that a flame is produced, the process is referred to as *burning* or *combustion.* A substance such as paper, gasoline, carbon disulfide, or natural gas, that readily bursts into flame and burns when heated or touched with a lighted match in the presence of oxygen or some other gaseous oxidizing agent, is said to be *combustible.* A combustible substance will spontaneously burst into flame in air, oxygen, or other oxidizing gas when it is heated to a temperature referred to as its *kindling temperature.* Each combustible substance has a definite kindling temperature, that of zinc ethyl, $Zn(C_2H_5)_2$, being so low that it will spontaneously burst into flame when placed in an open dish at room temperature. White phosphorous kindles at about 30°C, but its allotrope, red phosphorus, has a kindling temperature of about 260°C.

3.11 Spontaneous combustion. When a combustible substance bursts into flame spontaneously without external application of heat it is said to undergo *spontaneous combustion.* For example, a piece of white phosphorous will spontaneously ignite when placed in the open air at room temperature (about 21°C). It oxidizes slowly in the air at 21°C according to the equation

$$4\,P + 5\,O_2 = P_4O_{10} + \text{heat}$$

The heat evolved in this reaction raises the temperature of the unoxidized phosphorus slightly. As a result it is oxidized at a faster rate, heat is generated at a faster rate than it can be radiated into the air or conducted away by the walls of the dish in which it rests, so the temperature rises some more. This cycle continues until finally the temperature reaches the kindling point; the unoxidized phosphorus then bursts into

flame. The lower the kindling temperature of a substance, the greater the chance that it may undergo spontaneous combustion. Sometimes, as when green-stored hay spontaneously ignites in barns or stacks, a series of exothermic reactions may be responsible for the rise of the temperature to the kindling point of the combustible material. In this instance the increase in temperature is largely the result of fermentation. The fermenting green hay deep in the mow is so well insulated by the outer layers of hay that the heat generated is only slowly conducted away, and hence remains to raise the temperature and thereby increase the rate of the exothermic fermentation process. As a result the temperature rises until finally it may reach the kindling point of the dry hay. A spontaneous fire will then occur. Rags soaked with linseed oil or paint may ignite spontaneously as a result of the heat generated by the oxidation, by oxygen in the air, of the oil.

3.12 Heat of combustion. The heat generated when a combustible substance burns in air or oxygen is referred to as the *heat of combustion*, and is generally expressed in units of calories per gram, Btu (British thermal units) per pound, or Btu per cubic foot. The heats of combustion, generally referred to as the *calorific values*, of average samples of some common fuels are given in Table 3.1.

TABLE 3.1

CALORIFIC VALUES OF COMMON FUELS

	Calorific value		
Fuel	Cal/g	Btu/lb	Btu/cu ft
Pine wood	4,200	7,500	
Soft coal	7,000	12,700	
Hard coal	7,400	13,500	
Fuel oil	10,300	18,700	
Natural gas			1,110
Coal gas			580
Water gas			300

3.13 Calorific values of foods. Utilization of food by the body involves, in part, oxidation of this food to carbon dioxide and water by the oxygen which is inhaled when we breathe. Just as oxidation of elements and compounds in the laboratory yields heat energy, so the oxidation of food in the body yields energy. This energy is necessary to maintain the temperature of the body, keep its organs operating properly, and enable the individual to do work. Different foods yield different amounts of energy and are accordingly said to have different *calorie values* or *calorific values*. Since excess food over and above that required

to supply the energy needs of the body is usually stored up as fat, the calorific value of a food is, to a certain extent, a measure of the tendency of that food to add weight to the body. That is why reducing diets abound in low-calorie foods.

The calorific values of some foods are given in Table 3.2.

TABLE 3.2

CALORIFIC VALUES OF SOME COMMON FOODS

Food	*Calorific value* (100 grams)	*Food*	*Calorific value* (100 grams)
Vegetables		Cereals	
Asparagus	23	Bread, white	260
Beans, baked	99	Oatmeal	359
Beans, green	37	Rice	350
Cabbage	25	Dairy products	
Carrots	40	Butter	733
Celery	19	Cheese, cheddar	368
Corn on cob	104	Ice cream	214
Cucumbers	13	Milk, whole	69
Lettuce	16	Meats, fish, and poultry products	
Onions	45	Bacon	531
Peas, green	92	Beef liver	132
Potatoes, sweet	121	Beefsteak	233
Potatoes, white	84	Chicken	125
Spinach	22	Codfish	70
Tomatoes	20	Eggs	158
Fruits		Ham	456
Apples	60	Lamb chops	359
Avocados	179	Pork chops	347
Bananas	96	Shrimp	111
Cantaloupes	20	Turkey	156
Dates	306	Miscellaneous foods	
Grapefruit	43	Apple pie	216
Grapes	76	Cake, iced devil's food	354
Oranges	48	Chocolate	560
Peaches	49	Doughnuts	425
Pears	64	Honey	319
Pineapples	57	Peanut butter	611
Prunes, dried	292	Sugar	398
Raisins	292		
Strawberries	36		

3.14 Flames. The *flame* that is formed when a combustible substance burns is nothing more than the region where the air and the gaseous substance meet and react with each other. So much heat is generated during this reaction that the products of the reaction and

some of the unreacted materials are heated to the point where they glow and emit light. The glowing of the incandescent material produces the flame. For example, when hydrogen gas issuing into the air from a tube is raised to its kindling temperature by contact with a lighted match it burns with the sort of flame shown in Figure 3.1. Within the flame this reaction is taking place:

$$2\,H_2 + O_2 = 2\,H_2O + \text{heat}$$

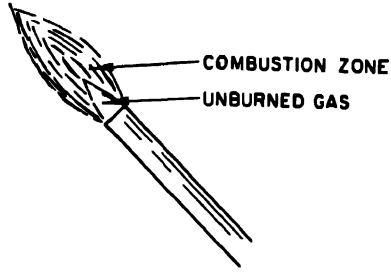


Figure 3.1. Flame of hydrogen gas burning in air.

The evolved heat does two things. It raises the molecules of H_2O, N_2, and unreacted O_2 and H_2 to the temperature where they glow, thereby producing the flame. Also, it raises the temperature of the succeeding molecules of hydrogen gas that escape from the tube to their kindling temperature, thereby keeping the flame going. Because it takes time to heat the issuing H_2 gas to its kindling point, an inner core of unburned hydrogen appears at the base of the flame. When the hydrogen has been completely oxidized and the gaseous materials have been chilled below the glow temperature by the cool outside air, the flame disappears. The flame of the ordinary laboratory burner, in which natural gas (mostly methane, CH_4) or some other carbon-rich fuel is used, is generated in the manner already explained for the hydrogen flame. The characteristic yellow-white color which is observed when the supply of air that is allowed to enter at the base of the burner is reduced results from the incandescence of the free carbon that is formed when the CH_4 molecules are thermally decomposed into carbon and hydrogen. This yellow-white flame is ordinarily referred to as a *luminous flame.*

3.15 Factors that influence the rate at which substances are oxidized by oxygen. The *rate* at which a substance reacts with oxygen gas will be influenced by the following factors.

A. *The Inherent Reactivity of the Substance.* If identical pieces of magnesium and iron are held in the Bunsen flame, the magnesium will take fire almost immediately, while the iron will only glow. If both pieces are removed from the flame and held in the air the magnesium will continue to burn rapidly until it is all oxidized to MgO. The iron, however, will soon quit glowing. If the two pieces of hot metal are removed from the flame and thrust into a flask of oxygen the iron burns at a moderately rapid rate but the magnesium will react at a terrific

rate and will flare up brightly. The magnesium is obviously much more *reactive* than iron, and as a result is oxidized much more rapidly. Under the same set of conditions calcium reacts more rapidly than magnesium, potassium reacts more rapidly than calcium, and copper reacts more slowly than iron. A series of carefully conducted experiments would show that the order of reactivity of the common metals with oxygen would be approximately as given in Table 3.3, the most reactive element falling at the top of the list.

TABLE 3.3

ORDER OF REACTIVITY OF THE COMMON METALS

Cesium
Rubidium
Potassium
Sodium
Barium
Strontium
Calcium
Magnesium
Aluminum
Manganese
Zinc
Chromium
Iron
Nickel
Tin
Lead
Hydrogen*
Copper
Mercury
Silver
Platinum
Gold

* Inserted for reference.

Because gold and platinum are not readily oxidized by oxygen or other nonmetals, they do not tarnish readily. As a result they retain their naturally attractive appearance in spite of exposure to the atmosphere. This is the main reason why they are so widely used in making jewelry, decorative metalware, and coins. Their comparative scarcity adds to their suitability for these uses. Because they are not easily tarnished, or as the ancient scientists might have put it, "corrupted," they, along with mercury and silver were and still are referred to as the *noble metals*. In contrast the other metals are referred to as *base metals*.

The order of reactivity of the nonmetals toward a common reactant, such as magnesium, would be approximately as represented in Table 3.4.

The term *reactive* as used in this section is not a very satisfactory one because it does not give us an *exact* measure of the quality that we are trying to describe; it simply tells us, in a general way, that a metal is easily oxidized or that a nonmetal readily oxidizes a metal. To state that an element is reactive is somewhat like answering the question, How tall is he? with the reply, He is quite tall. A better answer would be, He is *exactly* 6 ft 8 in. tall. There are exact terms (electropositivity, electronegativity, oxidation potential) for representing the ease with which an element reacts, and they will be used later. For the present, however, we are not prepared to understand the concepts on which

these exact terms are based. Accordingly we will speak about the *reactivity* of an element even though the term is admittedly indefinite.

B. *The Temperature.* The higher the temperature the more rapid the rate of reaction. A cold piece of iron wire placed in a flask of oxygen gas will oxidize (rust) slowly, but a hot piece of iron will burn rapidly. The spoilage of food is largely the result of chemical reactions. In warm weather these reactions proceed rapidly and the food spoils quickly. When the food is refrigerated the reactions are slowed down to the point where spoilage is prevented.

TABLE 3.4

ORDER OF REACTIVITY OF NONMETALS

Fluorine
Oxygen
Chlorine
Bromine
Sulfur
Nitrogen
Carbon
Selenium
Iodine
Phosphorus
Tellurium
Arsenic
Boron
Silicon

C. *Concentration of the Oxygen.* By concentration of a substance is meant *the quantity of that substance in a definite quantity* (either weight or volume) *of material.* If 100 g of mixture of oxygen and nitrogen contained 10 g of oxygen and 90 g of nitrogen, the amount of oxygen present would be 10 g but the concentration would be 10 g per 100 g of mixture; concentration is always expressed in units of quantity of substance per definite quantity of material, and not simply as quantity of substance. If the 10 g of oxygen were mixed with 40 g of nitrogen, the amount of oxygen would be the same as in the first example but the concentration would be 10 g per 50 g of mixture, or twice as great. Concentration can be expressed in various units such as per cent by weight, which means parts by weight of substance per 100 parts by weight of material, per cent by volume, grams of substance per specific number of grams of material, grams of substance per unit volume of material, etc. For example, we have been told that air contains 21% of oxygen by volume. That means that the concentration of the oxygen in air is 21 cc of oxygen per 100 cc of air, or 21 l of oxygen per 100 l of air, or 21 volumes of oxygen per 100 volumes of air. It should be noted that the concentration of *pure* oxygen gas at a pressure of 0°C and 2 atm would be twice as great as its concentration at 0°C and 1 atm, because a given weight of pure oxygen gas would occupy only half the volume at 2 atm and 0°C that it would at 1 atm and 0°C.

At a given temperature *the rate at which a substance reacts with oxygen increases as the concentration of the oxygen increases.* This is illustrated by the fact that a splint burns a great deal faster in pure oxygen than

it does in air. We shall find that this dependence of the rate on the concentrations of the reacting substances is characteristic of all chemical reactions. The exact nature of this dependence will be discussed in detail in Chapter 10.

D. *Total Amount of Solid Surface Per Unit Mass of Solid Reacting Substance.* If a stick of wood is split up into fine kindling it will burn a great deal faster than if it is left as a solid stick. The reason is that the total amount of wood surface per unit mass of wood has been greatly increased. In order to react with the wood the oxygen in the air must come in contact with it. That means that all burning takes place at the surface. Therefore, the greater the amount of surface, the greater the number of wood particles that will come in contact with oxygen and the faster the mass of wood will be burned up. Powdered coal is widely used as an industrial fuel; because it is finely divided and has a large amount of surface per unit mass it burns rapidly and gives off a lot of heat in a short time. As a result higher temperatures can be obtained than are possible with ordinary lump coal.

Dust explosions, which have occurred in coal mines, flour mills, grain elevators, starch factories, and carbon black plants, may take place when a match is lighted or an electric switch creates a spark in air which carries a high concentration of very finely divided oxidizable material. Because the dust is extremely finely divided the total surface per unit mass of material is enormous. As a result, when the match is lighted the dust in the immediate area will burn so rapidly that heat will be generated so fast that the adjacent layers of dust will take fire. This, in turn, will ignite the next layer, and so on until, within a few seconds, the fire has spread through all the air in the room or building. Because the reaction takes place so rapidly and the resultant heat is evolved so quickly, the temperature of the gases in the room (the nitrogen in the air and the steam, carbon dioxide, and carbon monoxide that are formed when the dust burns) will rise very quickly. This causes the gases to expand so rapidly and develop such high pressures that the entire building may be blown apart. The conditions that prevail in a dust explosion illustrate the conditions that must be present in any *explosion reaction*, namely, *a very rapid, highly exothermic process yielding gaseous products.*

E. *Adsorption of the Reacting Gases on a Catalytic Surface.* When a stream of hydrogen gas is directed at a quantity of cold, very finely divided platinum metal suspended on asbestos and placed in the open air, the platinum very quickly becomes red hot and the stream of hydrogen gas is ignited. Hydrogen gas and oxygen gas from the air are both *adsorbed* on the surface of the platinum; that is, they are attracted

to the surface and are caused to cling to it. At the same time they are somehow made more reactive. The molecules of the two gases, thus made more reactive and brought very close together on the surface of the platinum, react more readily and more rapidly than they normally would at the same temperature if they existed together as a gas mixture. The accumulating heat of the reaction, $2\,H_2 + O_2 = 2\,H_2O +$ heat, raises the temperature of the platinum and soon causes it to become red hot. This raises the surrounding hydrogen gas to its kindling temperature and it bursts into flame. The platinum is said to act as a *catalyst* because it causes the reaction to proceed at a faster-than-normal rate but does not itself react.

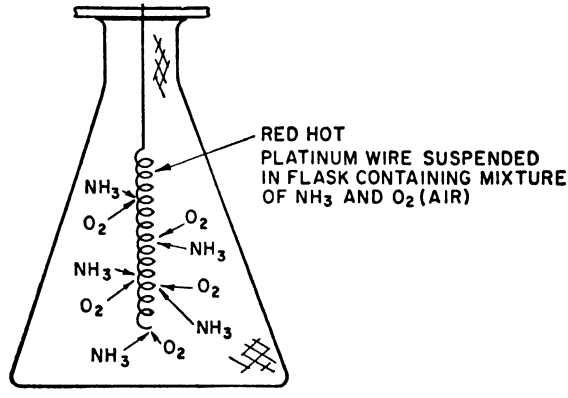


Figure 3.2. Catalytic oxidation of NH_3 by O_2 on surface of platinum wire.

If a piece of platinum wire is heated red hot and is then suspended in a flask containing a mixture of air and ammonia (NH_3) gas (see Figure 3.2), the wire continues to glow as long as there is ammonia and air in the flask even though no external heat is applied to it. A periodic examination of the contents of the flask will show that NO gas and steam are being formed and that the ammonia and oxygen are being used up. The O_2 and NH_3 molecules are being adsorbed on the surface of the hot platinum wire, and as a result they react readily according to the equation

$$4\,NH_3 + 5\,O_2 = 4\,NO + 6\,H_2O + \text{heat}$$

The heat that is evolved is transmitted to the platinum wire and keeps it red hot. The NO and H_2O molecules are not adsorbed by the platinum, but escape into the surrounding space, thereby allowing more NH_3 and O_2 molecules to be adsorbed, and the reaction to continue.

There is on the market a cigarette lighter which consists of a perforated cylinder containing finely divided platinum suspended on asbestos. Attached to the end or side of this cylinder is a wick which is kept soaked with methyl alcohol (CH_3OH) or some other combustible, volatile liquid (see Figure 3.3). When not in use the cylinder is kept in an airtight tube; the air in this tube is obviously saturated with alcohol vapor. To operate the lighter the cylinder is simply withdrawn from the tube. Quickly, and to all appearances, mysteriously, the wick bursts

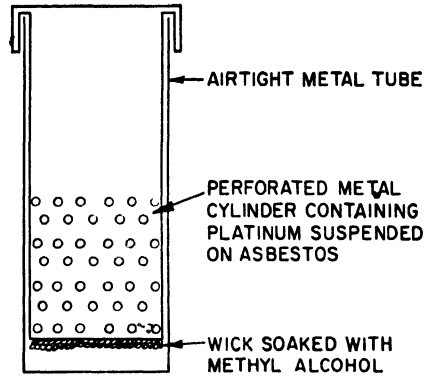


Figure 3.3. Cross section of a catalytic lighter.

into flame. To extinguish the lighter the cylinder is thrust back into the tube. What happens is simply this; the CH_3OH and O_2 (from air) molecules are adsorbed on the surface of the platinum, where they begin to react catalytically at room temperature as follows:

$$2\,CH_3OH + 3\,O_2 = 2\,CO_2 + 4\,H_2O + \text{heat}$$

The heat raises the temperature of the platinum, which speeds up the reaction, which causes the platinum to become hotter and hotter. The CO_2 and H_2O molecules escape from the surface of the platinum, thereby allowing more CH_3OH and O_2 molecules to be adsorbed and the reaction to go on. Finally the kindling temperature of the CH_3OH vapors which surround the asbestos and the wick is reached, and they burst into flame. Continued burning of the alcohol in the wick requires the presence of air. When the burning wick is thrust back into the airtight container the supply of air is cut off and the flame dies.

A large number of industrial gas-phase reactions are surface-catalyzed in the manner illustrated in the three examples given above. Some of these will be discussed later.

3.16 Heats of formation of the metal oxides. The heat that is evolved or absorbed when a compound is formed from its elements is referred to as the *heat of formation.* It is expressed in units of calories per gram or calories per mole. The heats of formation of the oxides of the metals are given in Table 3.5.

TABLE 3.5

HEATS OF FORMATION AND MELTING POINTS OF METAL OXIDES

Order of reactivity of metal	*Formula of oxide*	*Heat of formation* (cal/mole)	*Melting point* (°C)
Rubidium	Rb_2O	78,900	
Potassium	K_2O	86,400	
Sodium	Na_2O	99,400	
Barium	BaO	133,400	1923
Strontium	SrO	141,100	
Calcium	CaO	151,900	2707
Magnesium	MgO	143,840	2642
Aluminum	Al_2O_3	133,000*	2045
Manganese	MnO	92,000	1650
Zinc	ZnO	83,170	
Chromium	Cr_2O_3	89,900*	1900
Iron	Fe_2O_3	65,500*	1560
Tin	SnO	68,400	1127 (SnO_2)
Lead	PbO	52,070	890
Hydrogen	H_2O	68,320	0
Copper	CuO	37,100	1026
Mercury	HgO	21,500	decomposes, 100
Silver	Ag_2O	7,300	decomposes, 300
Platinum	PtO	7,000	
Gold	Au_2O_3	6,400*	decomposes, 160

* Calories per gram-atom of oxygen in the oxide.

An examination of the table shows that the oxides of the less reactive metals (Hg, Ag, Pt, Au) have relatively low heats of formation, while the oxides of the more reactive ones have high values. To decompose a compound into its elements one must add to it the same amount of energy that was given off when it was formed from these elements. It follows that the oxides of the noble metals are unstable, while the oxides of the more reactive metals are very stable toward heat.

3.17 Heats of formation of the nonmetal oxides. Table 3.6 lists the heats of formation of some nonmetal oxides. Here the trend is for the heat of formation to increase as the reactivity of the nonmetal decreases. This is in direct contrast to what was found to be true of the metal oxides.

TABLE 3.6

HEATS OF FORMATION AND MELTING POINTS OF NONMETAL OXIDES

Order of reactivity of nonmetal	*Formula of oxide*	*Physical state at room temp.*	*Heat of formation* (cal/mole)	*Melting point* (°C)
Fluorine	F_2O	gas	−5,500	−223.8
Chlorine	Cl_2O	gas	−18,200	−20
Sulfur	SO_2	gas	35,380*	−72.7
Nitrogen	N_2O_5	solid	2,000*	30
Carbon	CO_2	gas	47,000*	sublimes, −55.6
Selenium	SeO_2	solid	27,000*	340
Iodine	I_2O_5	solid		decomposes, 300
Phosphorus	P_2O_5	solid	72,000*	569
Tellurium	TeO_2	solid	38,800*	450
Arsenic	As_2O_3	solid	52,000*	sublimes, 218
Boron	B_2O_3	solid	100,700*	577
Silicon	SiO_2	solid	102,500*	1700

* Calories per gram-atom of oxygen.

3.18 Reactions of metal oxides with water. If the oxides of the metals are added to water the following experimental observations are noted:

1. The oxides of the seven most reactive metals (Table 3.3) react with water to form the metal hydroxides. The oxides of all metals below calcium in Table 3.3 react to such a slight extent that for all practical purposes they do not react with water or dissolve in it. The reactions that take place are:

$$Cs_2O + H_2O = 2\ CsOH$$
$$Rb_2O + H_2O = 2\ RbOH$$
$$K_2O + H_2O = 2\ KOH$$
$$Na_2O + H_2O = 2\ NaOH$$
$$BaO + H_2O = Ba(OH)_2$$
$$SrO + H_2O = Sr(OH)_2$$
$$CaO + H_2O = Ca(OH)_2$$

2. CsOH, KOH, RbOH, and NaOH are very soluble in water; $Ba(OH)_2$, $Sr(OH)_2$, and $Ca(OH)_2$ are moderately soluble.

3. The solution which is formed when the metal oxide reacts with water turns red litmus paper blue. Litmus paper is an *indicator* which turns blue in the presence of substances called *bases* and red in the presence of substances called *acids*. Therefore the metal hydroxides are bases, the oxides of metals are basic oxides, and metals are base-forming elements. A detailed study of bases will be made in Chapter 13.

3.19 Reactions of nonmetal oxides with water. If the oxides of the nonmetals are added to water the following experimental observations are noted:

1. All the oxides listed in Table 3.6 except SiO_2 are readily soluble or slightly soluble in water.

2. The solutions obtained by dissolving the nonmetal oxides in water all turn blue litmus paper red, showing that acids have been formed. This means that nonmetals form acidic oxides and the nonmetals are acid-forming elements.

The reactions that take place and the names of the acids formed are indicated in the equations given below.

$$Cl_2O + H_2O = 2\,HClO \text{ (hypochlorous)}$$
$$N_2O_5 + H_2O = 2\,HNO_3 \text{ (nitric)}$$
$$SO_2 + H_2O = H_2SO_3 \text{ (sulfurous)}$$
$$CO_2 + H_2O = H_2CO_3 \text{ (carbonic)}$$
$$SeO_2 + H_2O = H_2SeO_3 \text{ (selenious)}$$
$$I_2O_5 + H_2O = 2\,HIO_3 \text{ (iodic)}$$
$$P_4O_{10} + 6\,H_2O = 4\,H_3PO_4 \text{ (phosphoric)}$$
$$TeO_2 + H_2O = H_2TeO_3 \text{ (tellurous)}$$
$$As_2O_3 + 3\,H_2O = 2\,H_3AsO_3 \text{ (arsenious)}$$
$$B_2O_3 + 3\,H_2O = 2\,H_3BO_3 \text{ (boric)}$$

The general equation for the process represented by the above reactions is

$$\text{oxide of a nonmetal} + \text{water} = \text{a ternary acid}$$

3.20 Laboratory sources of oxygen. The laboratory sources of an element or compound, as they will be discussed in this book, include those sources that can be used in the laboratory by students for preparing and collecting quantities of the substance for use in determining its physical and chemical properties, and those sources that are of interest because of the principles that they illustrate or properties that they emphasize even though, for one reason or another, they are not suitable for use in preparing and collecting quantities of the substance in the laboratory.

The important laboratory sources of oxygen are:

A. *Heating the Oxides of the Noble Metals, Mercury and Silver.* As has already been pointed out, the oxides of the noble metals are so unstable that they decompose on moderate heating. The products formed are oxygen gas and the free metal. The word and balanced equations for the reactions involved when HgO and Ag_2O are heated are:

mercury(II) oxide (heated) = mercury + oxygen
$2\,HgO \quad = 2\,Hg + O_2$

silver oxide (heated) = silver + oxygen
$2\,Ag_2O \quad = 4\,Ag + O_2$

B. *Catalytic Decomposition of Hydrogen Peroxide*, H_2O_2. Hydrogen peroxide is quite unstable, decomposing slowly at 80–90°C to give water and oxygen.

$$2\,H_2O_2\ (\text{heated}) = 2\,H_2O + O_2$$

This decomposition reaction is so strongly catalyzed by certain substances, such as powdered manganese dioxide (MnO_2) and finely divided platinum, that a pinch of these substances added to hydrogen peroxide in a flask or beaker at room temperature produces a rapid evolution of oxygen gas. The platinum and MnO_2 remain in the beaker apparently unchanged; since they speed up the rate but are not changed as a result of the reaction they are, according to the definition previously given, referred to as *catalysts*.

When hydrogen peroxide is applied as an antiseptic to a freshly cut wound it bubbles profusely because its decomposition into H_2O and O_2 is being catalysed by some substance present in blood.

C. *Heating the Dioxides and Peroxides of Certain Metals*

lead dioxide (heated) = lead oxide + oxygen
$2\,PbO_2 \quad = 2\,PbO + O_2$

Although PbO, in which lead has an oxidation number of +2, is very stable and cannot be decomposed by heating in the laboratory, PbO_2, in which the oxidation number of lead is +4, is quite unstable. When PbO_2 is heated the lead changes to its more stable oxidation state, +2.

barium peroxide (heated) = barium oxide + oxygen
$2\,BaO_2 \quad = 2\,BaO + O_2$

The peroxides of the metals (BaO_2, CaO_2, SrO_2, Na_2O_2, ZnO_2) may be looked upon as having been formed from hydrogen peroxide by replacement of the hydrogen in the H_2O_2 molecule by metal. Thus H_2O_2 yields BaO_2. Since H_2O_2 is decomposed by heat into hydrogen oxide (H_2O) and oxygen it is not surprising to find that the metal peroxides yield the metal oxide and oxygen.

D. *Catalytic Decomposition of Heated Bleaching Powder*, $CaCl_2O$.

$$2\,CaCl_2O\ (\text{heated}) = 2\,CaCl_2\ (\text{calcium chloride}) + O_2$$

A suspension of bleaching powder in water is heated; the reaction is catalyzed by cobalt oxide. The details of the laboratory procedure for

this and subsequent laboratory methods are given in most laboratory manuals.

E. *Heating the Chlorate of an Active Metal* (see Figure 3.4). Potassium chlorate ($KClO_3$) or sodium chlorate ($NaClO_3$) is generally used. The reaction is catalyzed by MnO_2 or Fe_2O_3.

$$2\ KClO_3\ (\text{heated}) = 2\ KCl + 3\ O_2$$

Potassium chlorate consists of potassium in combination with the chlorate radical, ClO_3. Since potassium has a valence of 1, the valence of the ClO_3 radical must also be 1.

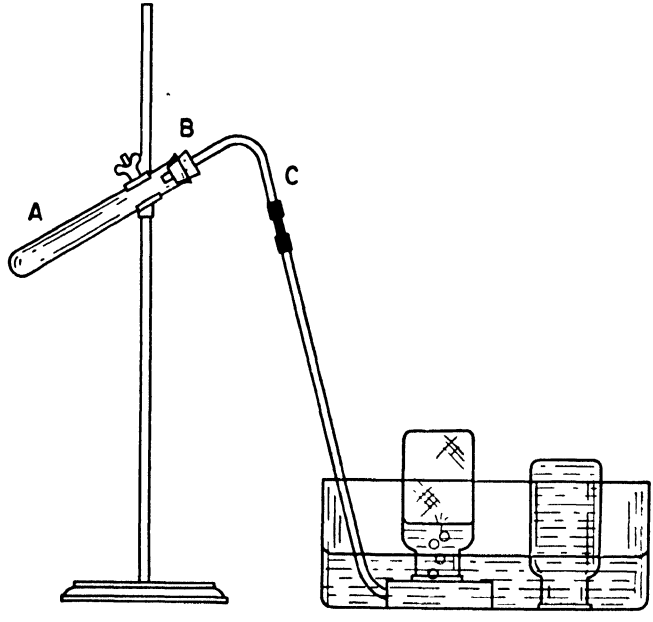


Figure 3.4. Apparatus for the laboratory preparation of oxygen by heating potassium chlorate. The $KClO_3$ is placed in test tube *A* into which is fitted the rubber stopper *B* carrying the delivery tube *C*. The oxygen gas that is evolved is collected by displacement of water.

F. *Heating the Nitrate of an Active Univalent Metal* (K, Na, Li, Rb, Cs).

$$2\ KNO_3\ (\text{potassium nitrate}) + \text{heat} = 2\ KNO_2\ (\text{potassium nitrite}) + O_2$$

G. *Reaction of Sodium Peroxide*, Na_2O_2, *with water*. Water is added, dropwise, to solid Na_2O_2 in a generator flask (see Figure 3.5). Oxygen gas is evolved according to the equation

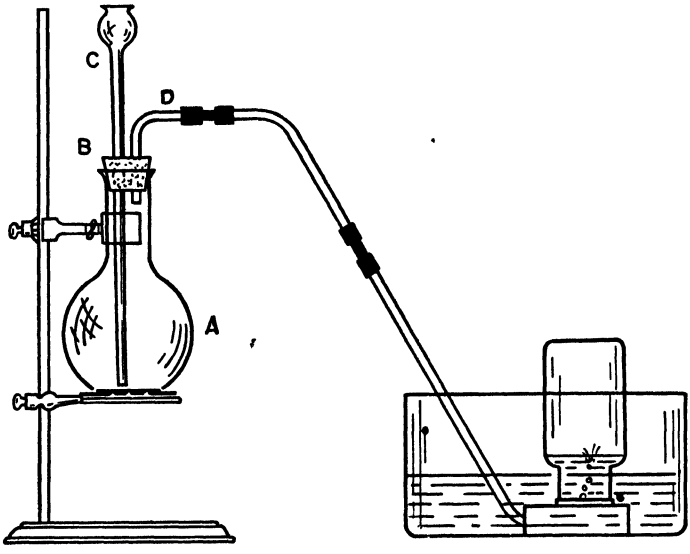


Figure 3.5. Laboratory preparation of oxygen from sodium peroxide. Solid Na_2O_2 is placed in flask *A* which is fitted with a rubber stopper *B* carrying a thistle tube *C* and delivery tube *D*. Water is added through the thistle tube. The oxygen which is evolved is collected by displacement of water.

$$2\ Na_2O_2 + 2\ H_2O = 4\ NaOH\ (\text{sodium hydroxide}) + O_2$$

3.21 Explanations for chemical facts. A study of the laboratory sources of oxygen raises questions such as: Why is PbO more stable than PbO_2? Why does $KClO_3$ decompose to give KCl when heated, while KNO_3 decomposes to give KNO_2? Why is the decomposition of H_2O_2 catalyzed by MnO_2 but not by PbO_2?

Similar questions will, and should, continually be raised as each new chapter is covered. Unfortunately, we do not know the correct answers to many of these questions. The experimental fact that PbO does not decompose when heated while PbO_2 does is undeniable. But why there is this difference no one can say *for certain*. We can list the facts that have been established by chemical experimentation, and on the basis of these facts, we can lay down certain *rules*, make certain *generalizations*, and propound certain *theories*. These rules, generalizations, and theories enable us to systematize chemical facts and thereby make it possible to predict what will happen to a specific substance under a specific set of conditions. When we find that a theory agrees with all facts and that all facts agree with the theory it becomes a *law*. We can then use the law to predict and explain facts that fall within its domain.

That we cannot answer the "why" or "how" questions pertaining to specific experimental facts does not deny these facts or make them any less valuable or important.

3.22 Commercial preparation of oxygen. Approximately 210,000 tons of oxygen are prepared in the United States each year, about 90% by fractional distillation of liquid air and 10% by electrolysis of water.

A. *Fractional Distillation of Liquid Air* (see Figure 3.6). Air con-

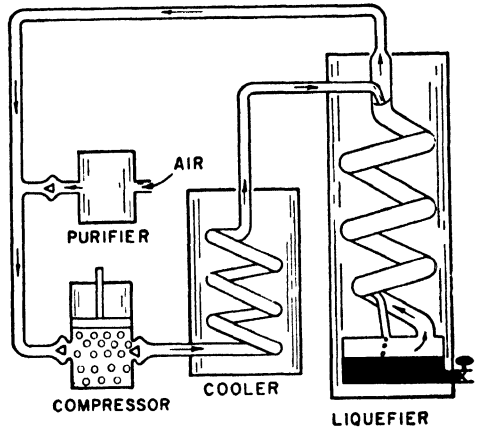


Figure 3.6. Liquefaction of air. The air is first purified to remove dust, moisture and carbon dioxide. It is then compressed after which it is cooled by cold water. This compression and cooling may be repeated two or more times to a final pressure of about 200 atmospheres. The highly compressed cooled air then passes into the liquefier where it is allowed to expand. This expansion absorbs heat and cools the air further. This cooled air is again recycled and compressed and cooled still further. In the recycling process the cold air that passes out of the liquefier through the larger outer coil cools the air that enters through the smaller inner coil. Eventually the temperature of the air in the liquefier falls so low that liquefaction begins and continues as long as the recycling is continued.

tains by volume about 21% oxygen and 79% nitrogen. At a pressure of 760 mm, liquid nitrogen boils at $-195°C$, while liquid oxygen boils at $-183°C$. Liquid air will boil at about $-190°C$ at 760 mm; the vapors that first escape are practically pure nitrogen, since it boils at a lower temperature than oxygen. That means that the residual liquid will be richer in oxygen than the original liquid air. As the boiling proceeds and the boiling temperature rises above $-190°$, the residual liquid becomes richer and richer in oxygen. At the same time, however, the

vapors also become richer in oxygen. The reason why some oxygen is present in the vapor at temperatures below its boiling point, −183°C is that it, like any liquid, has a definite vapor pressure at temperatures below its boiling point. However, the per cent of the less volatile oxygen in the vapor phase will always be less than its per cent in the liquid with which it is in boiling equilibrium, and the per cent of the more volatile nitrogen will always be greater in the vapor phase than in the liquid phase. If the nitrogen-rich vapors are condensed again, by cooling, and the resulting liquid is again boiled, the residual liquid will again be richer in oxygen than the escaping vapor. If this cycle of distillations and redistillations is repeated many times, practically pure oxygen remains as a residual liquid. The cycle of redistillations is referred to as *fractional distillation*. The commercial fractional distillation of air is carried out in *fractionation columns* many feet tall. Practically pure nitrogen is collected at the top of the column, while 99.5% liquid oxygen is withdrawn at the bottom.

B. *Electrolysis of Water*. When an electric current is passed through water, hydrogen gas is liberated at the negative pole and oxygen gas at the positive pole (see Figure 3.7). Obviously, this method serves for the preparation of both pure oxygen and pure hydrogen. The over-all reaction that takes place is

$$2\,H_2O + \text{electric current} = 2\,H_2 + O_2$$

Pure water is practically a nonconductor of electricity, so a small amount of sulfuric acid (H_2SO_4) is added to give a conducting solution. The mechanism by which H_2SO_4 causes water to become a conductor will be discussed in Chapter 15.

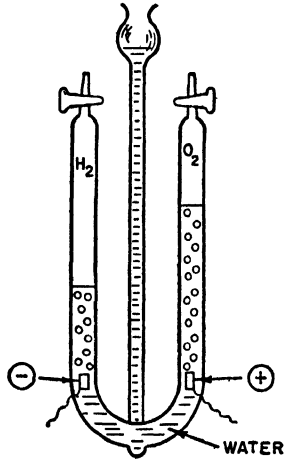


Figure 3.7. Electrolysis of water. The electrodes are of platinum. The volume of the hydrogen evolved is twice that of the oxygen.

The commercial oxygen manufactured by the above processes is marketed and distributed as either liquid or gaseous oxygen.

3.23 Uses of oxygen. The most important commercial uses of oxygen, aside from its use, in the form of air, in all animal and plant respiratory processes and in all household and industrial stoves and furnaces are:

1. *Oxyacetylene and oxyethylene welding and cutting.* Acetylene (C_2H_2) or ethylene (C_2H_4) gas is burned in an atmosphere of oxygen, the combustion being carried out in a specially designed torch (see Figure 3.8). Because C_2H_2 and C_2H_4 have very high heats of combustion and because the use of pure oxygen causes the reaction to proceed at a very

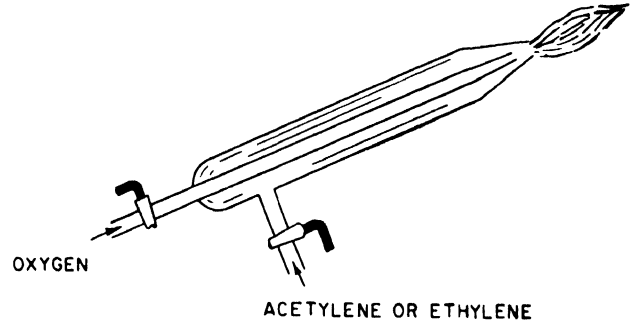


Figure 3.8. The oxyacetylene or oxyethylene blowtorch.

rapid rate, temperatures of 3000°C and higher are reached. At these temperatures iron, steel, and other metals and alloys are readily and quickly melted.

$$2\,C_2H_2 + 5\,O_2 = 4\,CO_2 + 2\,H_2O + \text{heat}$$
$$C_2H_4 + 3\,O_2 = 2\,CO_2 + 2\,H_2O + \text{heat}$$

2. *Enrichment of the air used in furnaces* for the manufacture of iron and steel and other industrial materials. As the per cent of oxygen in the air increases, the rate at which coal is burned by this air increases, and the temperature attained increases. This increase in temperature speeds up the rate of the complex reactions involved in the conversion of iron ore to steel, and as a result cuts down the time required to prepare a ton of iron or steel. The monetary gain resulting from this speed-up offsets the cost of the oxygen used.

3. *As a raw material* in the manufacture of various chemical compounds.

4. *High-altitude flying.* Because of the low density of the air at high altitudes, the amount of oxygen inhaled in each breath is not sufficient to sustain normal human activity. Therefore a supply of oxygen is necessary.

5. *In hospitals,* by patients suffering from respiratory diseases, heart attacks, etc.

Questions and Problems

1. Define or describe and illustrate each of the following: oxidation, oxidizing agent, oxidation state, oxidation number, law of multiple proportion, burning, combustion, combustible substance, kindling temperature, spontaneous combustion, heat of combustion, calorific value, flame, noble metal, base metal, concentration, adsorption, catalyst, heat of formation, base, basic oxide, acid, acidic oxide, fractional distillation, electrolysis, explosion.

2. Give five sources of oxygen. Illustrate the preparation of oxygen from each specific source by a balanced chemical equation.

3. Give balanced chemical equations to illustrate two laboratory methods for preparing oxygen. Include a sketch of the apparatus which you would use.

4. Describe two commercial methods for preparing oxygen.

5. Complete the following statements and illustrate each with a balanced chemical equation.

(a) oxide of a noble metal (heated) =
(b) oxide of active metal + water =
(c) oxide of a nonmetal + water =
(d) chlorate of metal (heated) =
(e) active metal + oxygen (heated) =
(f) nitrate of active monovalent metal (heated) =
(g) peroxide of metal (heated) =
(h) combustible compound + oxygen (heated) =
(i) nonmetal + oxygen (heated) =

6. What factors determine how fast a chemical reaction will proceed?

7. What are the requirements for an explosion reaction?

8. How is the stability of a metal oxide related to
(a) the chemical reactivity of the metal?
(b) the heat of formation of the oxide?

9. Give the oxidation number of the element set in boldface: $H_2\mathbf{O}$; $\mathbf{Fe}_2O_3$; $\mathbf{N}O_2$; $K\mathbf{Cl}O_3$; $H_3\mathbf{B}O_3$; $\mathbf{As}_2O_5$; $H_2\mathbf{S}$; $H_3\mathbf{P}O_4$; $\mathbf{Zn}Cl_2$.

10. How would you demonstrate that MnO_2 catalyzes the decomposition of $KClO_3$?

11. Why cannot pure O_2 be obtained from liquid air?

12. Point out the relationship between oxidation and change in oxidation number.

13. How could you demonstrate, in the laboratory (a) that calcium is a metal; (b) that sulfur is a nonmetal? Give equations for all reactions.

14. Show, by balanced chemical equations, what happens when each of the following combustible substances is burned in oxygen or air: S; C; H_2; Mg; B; Si; H_2S; CH_4; C_2H_2; C_2H_4; $C_6H_{10}O_5$; C_2H_5OH; $(CH_3)_3BO_3$; SiH_4; $Mg(C_2H_5)_2$; $Pb(C_2H_5)_4$; $C_{12}H_{22}O_{11}$.

15. List three important commercial uses of oxygen.

16. How would you distinguish between the two substances in each of the following pairs. In each case tell what you do and what you observe that enables you to make the distinction, and write balanced equations for the reactions that take place.

(a) Two black oxides, one Ag_2O, the other NiO
(b) Two white solids, one $KClO_3$, the other KCl
(c) Two white solids, one ZnO, the other BaO_2
(d) Two white solids, one CaO, the other P_4O_{10}
(e) Two bright, shiny metals, one Pt, the other Mg
(f) Two colorless gases, one O_2, one air

17. Compare and contrast metals and nonmetals with respect to: (a) relationship between the reactivity of the element and the heat of formation of its oxide; (b) reaction of their oxides with water.

18. How many grams of carbon are there in 40 l of CO gas collected over water at 18°C and 746 mm?

CHAPTER 4

Hydrogen

4.1 Occurrence and importance. Hydrogen is one of the most widely distributed of the chemical elements, being a constituent of more than 500,000 different compounds. In combination with oxygen it forms the most plentiful compound in the world, water (H_2O). In combination with carbon in a series of compounds called hydrocarbons it constitutes the world's supply of petroleum and natural gas. In combination with oxygen and carbon in the form of cellulose it makes up the major part of the fibrous structure of all the trees, shrubs, plants, and grasses on the earth. In combination with these same two elements as well as nitrogen and an occasional other element, it forms the chemical substances called proteins; these proteins make up the major part of all lean animal tissue and represent a substantial part of seeds and cereal grains. In combination with oxygen and carbon it constitutes the animal and vegetable fats as well as the sugars and the various essences that give fruits and flowers their distinctive tastes and odors. Hydrogen gas is never found free in nature except in very small amounts in the region of volcanoes.

4.2 Identification. When a mixture of hydrogen and air is ignited an explosion occurs, by the reaction

$$2\,H_2 + O_2 = 2\,H_2O + \text{heat}$$

This provides a simple and striking test for identifying the presence of *small quantities* of the gas. Because of the violence of the explosion it should not be used on large volumes of gas.

4.3 Physical properties. Hydrogen is a colorless, odorless, and tasteless gas. Its density of 2.016 g/22.4 l makes it the lightest of all gases and shows that its molecule is diatomic (H_2). It has a critical temperature of —239.9°C and a critical pressure of 12.8 atm, and is therefore very difficult to liquefy. The liquefied product, which boils at −252.7°C at a pressure of 1 atm, is the lightest known liquid, with a density of 0.07 g/cc.

Hydrogen gas is very slightly soluble in water and can therefore be collected by displacement of water. Since it is about 14.4 times lighter

than air and tends therefore to rise rapidly in air, the bottles in which it is stored when prepared in the laboratory are placed on the desk mouth down.

4.4 Chemical properties. Hydrogen combines directly with most nonmetals when heated to form stable binary compounds. It also forms stable hydrides with the more active metals. Its affinity for the nonmetals, particularly for oxygen and sulfur, is so great that under proper conditions it will remove them from their combination with other elements.

A. *Reaction with Nonmetals.* The reactions that take place and the heats of formation of the resulting compounds are given in Table 4.1.

TABLE 4.1

HYDROGEN COMPOUNDS OF NONMETALS

Order of reactivity of nonmetal	*Equation for formation*	*Physical state of compound at room temperature*	*Heat of formation* (cal/mole)
Fluorine	$H_2 + F_2 = 2\ HF$	gas	64,200
Oxygen	$2\ H_2 + O_2 = 2\ H_2O$	liquid	57,798
Chlorine	$H_2 + Cl_2 = 2\ HCl$	gas	22,063
Bromine	$H_2 + Br_2 = 2\ HBr$	gas	8,660
Sulfur	$H_2 + S = H_2S$	gas	4,815
Nitrogen	$3\ H_2 + N_2 = 2\ NH_3$	gas	21,040
Carbon	$2\ H_2 + C = CH_4$	gas	17,889
Selenium	$H_2 + Se = H_2Se$	gas	−20,500
Iodine	$H_2 + I_2 = 2\ HI$	gas	−6,200
Phosphorus	PH_3*	gas	−2,210
Tellurium	$H_2 + Te = H_2Te$	gas	−36,900
Arsenic	AsH_3*	gas	−41,000
Boron	BH_3*	gas	−7,500
Antimony	SbH_3*	gas	−34,000
Silicon	SiH_4*	gas	14,800

* Cannot be prepared by direct combination of hydrogen with the nonmetal; obtained by indirect methods.

Hydrogen combines with F_2, O_2, and Cl_2 with explosive violence. Combination with N_2, Br_2, I_2, C, S, Se, and Te takes place slowly and only at high temperatures.

By analogy with H_2O, in which it has an oxidation number of +1, the oxidation number of hydrogen in all these compounds is +1. In each of the reactions in Table 4.1 hydrogen is oxidized and the nonmetal functions as the oxidizing agent. The oxidation number of the nonmetal is negative in each of the hydrogen compounds.

B. *Reaction with Reactive Metals.* The more reactive metals, Li, K,

Rb, Cs, Ba, Sr, Ca, and Na, combine directly with hydrogen at high temperatures to form solid hydrides of moderate stability. Hydrides of

$$2\ Na + H_2 = 2\ NaH$$

the less reactive metals have not been prepared. The fact that the hydrides of the metals are solids, whereas the compounds with the nonmetals, except H_2O, are gases suggests that the hydrides of the metals fall in the same category of compounds as the oxides of the metals. Since the metals have positive oxidation states in their oxides, they can also be presumed to have positive oxidation states in their hydrides. That means that the oxidation number of hydrogen in the metal hydrides is -1. This conclusion is supported by the experimental fact that, when a direct current is passed through a molten hydride such as LiH, hydrogen gas collects at the positive electrode.

C. *Reaction with Compounds. Reduction.* Because the tendency of hydrogen to react with certain of the nonmetals is very great, it will remove them from their compounds. This property of hydrogen is well illustrated by its reaction with the oxide of a metal such as CuO. When hydrogen is passed over heated copper oxide, the latter is converted to free copper, and water vapor is formed. The reaction is

$$CuO + H_2 = Cu + H_2O$$

Similar reactions will occur when hydrogen is passed over heated PbO, SnO, and Fe_2O_3; however, as the reactivity of the metal increases, the temperature required to bring about the reaction increases. The oxides of metals more reactive than zinc cannot be made to react with hydrogen at the highest temperatures attainable in the laboratory.

It will be noted, in the reaction of H_2 with CuO, that the oxidation number of copper is reduced from $+2$ in CuO to 0 in free Cu. The copper is therefore said to be *reduced*, and the chemical process is called *reduction*. Because hydrogen is responsible for the reduction of the copper from an oxidation state of $+2$ to a state of 0, it is referred to as the *reducing agent*. In terms of the above equation, and all similar equations, we can state that *reduction is a chemical process in which the oxidation number of an element is reduced; when the oxidation number of an element has been reduced, a reduction reaction has taken place.*

We will note, in the above reaction, that not only has the oxidation number of copper been reduced from $+2$ to 0, but the oxidation number of the hydrogen, which is the reducing agent, has been increased from 0 in H_2 to $+1$ in H_2O. That means that, by our previous definition, hydrogen has been oxidized. Since the CuO is responsible for the oxidation of the H_2 to H_2O, it is the oxidizing agent. If we examine the balanced

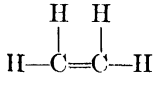
equation we find that 1 gram-atom of copper has its oxidation number reduced from +2 to 0 for a total decrease of 2. At the same time 2 gram-atoms of hydrogen have their oxidation numbers increased from 0 to +1 for a total increase of 2. That means that in the chemical process *the total increase in oxidation number on the part of the element oxidized is equal to the total decrease in oxidation number on the part of the element reduced.*

If we go back and examine the balanced equations for the oxidation reactions that were presented in Chapter 3 we will find that *in each case where an element is oxidized, that is, has its oxidation number increased, another element is reduced, that is, has its oxidation number decreased, and the total increase in oxidation number of the element oxidized is equal to the total decrease in oxidation number of the element reduced.* To illustrate, in the reaction

$$2\,Mg + O_2 = 2\,MgO$$

magnesium is oxidized from an oxidation number of 0 in Mg to +2 in MgO, and oxygen is reduced from an oxidation number of 0 in O_2 to −2 in MgO. The total increase in oxidation number of the 2 gram-atoms of magnesium is 4, and the total decrease in oxidation number of the 2 gram-atoms of oxygen is also 4. Oxygen gas is the oxidizing agent and magnesium is the reducing agent. The results of a similar analysis of several of the other reactions presented in Chapter 3, are given in Table 4.2. Since in all reactions of this type both oxidation and reduction occur, they are referred to as *oxidation-reduction reactions* or, more simply, *redox reactions.*

D. *Addition of Hydrogen to Unsaturated Carbon Compounds.* In a great many carbon compounds the carbon atoms are not combined with so many atoms of other elements as their valence of 4 would allow. Thus in the compound C_2H_4, whose structural formula can be represented as



each carbon atom has one unsatisfied valence bond. Such compounds are said to be *unsaturated.* Most of these unsaturated compounds will combine with additional hydrogen to form *saturated* compounds, that is, compounds in which the carbon valences are completely satisfied. The chemical process involved is called *hydrogenation.*

Hydrogenation of unsaturated carbon compounds is of great industrial importance and plays a dominant role in the manufacture of such materials as motor fuels, synthetic rubber, plastics, and vegetable shortening materials. Most hydrogenation reactions are carried out at high pressures and are surface catalyzed, finely divided nickel being the most

TABLE 4.2

ANALYSIS OF SOME OXIDATION-REDUCTION REACTIONS

Equation for reaction	For the element oxidized				For the element reduced				Oxidizing agent	Reducing agent
	Element	Initial oxidation number	Final oxidation number	Total increase in oxidation number	Element	Initial oxidation number	Final oxidation number	Total decrease in oxidation number		
$2\,Ca + O_2 = 2\,CaO$	Ca	0	+2	4	O	0	−2	4	O_2	Ca
$4\,Na + O_2 = 2\,Na_2O$	Na	0	+1	4	O	0	−2	4	O_2	Na
$4\,Al + 3\,O_2 = 2\,Al_2O_3$	Al	0	+3	12	O	0	−2	12	O_2	Al
$S + O_2 = SO_2$	S	0	+4	4	O	0	−2	4	O_2	S
$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O$	C	−4	+4	8	O	0	−2	8	O_2	CH_4
$CS_2 + 3\,O_2 = CO_2 + 2\,SO_2$	S	−2	+4	12	O	0	−2	12	O_2	CS_2
$Mg + Cl_2 = MgCl_2$	Mg	0	+2	2	Cl	0	−1	2	Cl_2	Mg
$3\,Mg + N_2 = Mg_3N_2$	Mg	0	+2	6	N	0	−3	6	N_2	Mg
$2\,CO + O_2 = 2\,CO_2$	C	+2	+4	4	O	0	−2	4	O_2	CO
$4\,NH_3 + 5\,O_2 = 4\,NO + 6\,H_2O$	N	−3	+2	20	O	0	−2	20	O_2	NH_3
$2\,CH_3OH + 3\,O_2 = 2\,CO_2 + 4\,H_2O$	C	−2	+4	12	O	0	−2	12	O_2	CH_3OH

widely used catalyst. The following reaction illustrates a simple hydrogenation process.

$$C_2H_4 \text{ (ethylene)} + H_2 = C_2H_6 \text{ (ethane)}$$

The partial hydrogenation of cottonseed oil to form a semisolid product such as Crisco or Dexo involves the following reaction.

$$\underset{\textit{liquid} \text{ glyceryl oleate}}{C_3H_5(C_{17}H_{33}COO)_3} + 3\,H_2 = \underset{\textit{solid} \text{ glyceryl stearate}}{C_3H_5(C_{17}H_{35}COO)_3}$$

4.5 The properties of the nonmetal binary hydrogen compounds. If the hydrogen compounds of the nonmetals are compared certain groups of them are found to be similar.

A. HF, HCl, HBr, HI. All are colorless gases, all have the same sharp, irritating odor, all produce strong fuming when brought in contact with moist air, and all are soluble in water and form solutions which react acidic to litmus paper. All have the same general formula in which the oxidation number of the halogen (F, Cl, Br, I) is -1. As already noted in Table 4.1 the heat of formation decreases as the reactivity of the halogen decreases, the values, in calories per mole, being: HF, 64,200; HCl, 22,063; HBr, 8,660; HI, $-6{,}200$. One is justified in concluding that fluorine, chlorine, bromine, and iodine are similar since they react with hydrogen to form similar halides.

B. H_2O, H_2S, H_2Se, H_2Te. The chemical formulas are similar; the O, S, Se, and Te each has an oxidation number of -2. Of these, H_2O is a liquid, but H_2S, H_2Se, and H_2Te are all gases, each with a somewhat similar foul odor. The solutions of H_2S, H_2Se, and H_2Te in water are weakly acidic. Here, as with the halogen compounds, the heat of formation decreases as the reactivity of the nonmetal decreases. The similarity between these four compounds is not so pronounced as between the halogen compounds but there most definitely is enough similarity to justify the conclusion that oxygen, sulfur, selenium, and tellurium are similar.

C. NH_3, PH_3, AsH_3, SbH_3. The chemical formulas are similar, and in each case the oxidation number of the nonmetal is -3. All are gases, and there is a definite similarity in the character of the odor of each.

D. CH_4 *and* SiH_4. Both are gases with high heats of formation. In each compound the oxidation number of the nonmetal is -4.

4.6 Laboratory sources of hydrogen. A. *Reaction of a Metal More Reactive than Hydrogen with an Acid.* A detailed discussion of the properties of acids will be given in Chapter 13. At this time we need to

note only that (a) their solutions turn blue litmus paper red (see Section 3.20), and (b) they all contain hydrogen in combination with a nonmetal or nonmetal radical (HCl, H_2SO_4, $HC_2H_3O_2$, HNO_3). This hydrogen can be replaced by a metal more reactive than hydrogen. (See the reactivity table of the metals, Table 3.3, page 80.) If the solution that remains when the metal has ceased reacting with the acid is evaporated to dryness, a solid compound called a *salt* remains. The word equation for the reaction is

$$\text{metal} + \text{acid} = \text{salt} + \text{hydrogen}$$

Table 4.3 lists some significant facts about three of the widely used common acids. The following reactions illustrate the liberation of hydrogen from these acids by some common reactive metals.

$$Ca + 2\,HCl = CaCl_2 + H_2$$
$$Zn + H_2SO_4 = ZnSO_4 + H_2$$
$$Mg + 2\,HC_2H_3O_2 = Mg(C_2H_3O_2)_2 + H_2$$
$$2\,Al + 6\,HCl = 2\,AlCl_3 + 3\,H_2$$
$$Fe + 2\,HCl = FeCl_2 + H_2$$
$$2\,Na + H_2SO_4 = Na_2SO_4 + H_2$$

TABLE 4.3

SIGNIFICANT FACTS ABOUT SOME COMMON ACIDS

Formula of acid	Chemical name	Common name	Acid radical			Formula and name of typical salt
			Formula	Name	Valence	
HCl	hydrogen chloride	hydrochloric	Cl	chloride	−1	NaCl, sodium chloride
H_2SO_4	hydrogen sulfate	sulfuric	SO_4	sulfate	−2	$ZnSO_4$, zinc sulfate
$HC_2H_3O_2$	hydrogen acetate	acetic	$C_2H_3O_2$	acetate	−1	$Mg(C_2H_3O_2)_2$, magnesium acetate

These reactions are commonly referred to as *replacement reactions;* one element replaces another in its compounds.

As already stated, any metal above hydrogen in the reactivity table will replace hydrogen from an acid. The more reactive the metal (the higher its position in the table) the more rapid the rate of its reaction with acids. Potassium and sodium react with such violence that their use is hazardous; magnesium reacts very rapidly but can be utilized;

zinc reacts at a moderately rapid rate, and is the metal most commonly used for laboratory preparation of hydrogen; tin and lead react so slowly that their use is impractical; copper and the other metals below hydrogen in the table fail generally to liberate hydrogen from acids.

The rate at which hydrogen is liberated by a specific metal varies from one acid to another. Thus magnesium reacts rapidly with HCl and H_2SO_4, but more slowly with $HC_2H_3O_2$ and H_3PO_4. The exact reason for this difference in behavior will be discussed in Chapter 13. For the present we can say that acids that react rapidly are said to be *strong*, while those that react slowly are *weak*.

In accordance with the principle already stated in Chapter 3, the rate at which a given metal reacts with a given acid increases as the temperature increases.

The rate at which a metal above hydrogen reacts with a certain acid is catalyzed by the presence of bits of some metal which lies below hydrogen in the reactivity table. For this reason copper is generally introduced as a catalytic agent when the reaction of zinc with sulfuric acid is used for laboratory preparation of hydrogen. The copper catalyst is generally deposited in a very finely divided condition on the surface of the zinc by replacing it from a solution of $CuSO_4$ ($Zn + CuSO_4 = ZnSO_4 + Cu$; this particular replacement reaction illustrates the general principle that a metal will replace a less reactive metal from a solution of its salts).

B. *Reaction of a Very Active Metal* (Li, K, Rb, Cs, Ba, Sr, Ca, *and* Na) *with Cold Water*. The word equation for the reaction is

$$\text{active metal} + \text{cold water} = \text{hydroxide of the metal} + H_2$$

Specific reactions are

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

In general, the greater the reactivity of the active metal, the more rapid the rate of the reaction. As already noted in Chapter 3, the hydroxides of the monovalent active metals (LiOH, KOH, RbOH, CsOH, and NaOH) are very soluble in water, while the hydroxides of the divalent active metals ($Ba(OH)_2$, $Sr(OH)_2$, and $Ca(OH)_2$) are only moderately soluble.

C. *Reaction of a Less Active Metal Above Hydrogen with Steam* to form the oxide of the metal and hydrogen. Specific reactions are

$$Mg + H_2O \text{ (heated)} = MgO + H_2$$
$$Zn + H_2O \text{ (heated)} = ZnO + H_2$$

The lower the reactivity of the metal, the higher the required temperature. Because of the high temperatures and complex equipment needed, this is not a practical laboratory source. Because the hydroxides of the less active metals are unstable at high temperatures, decomposing to give the oxide of the metal and water [$Mg(OH)_2 = MgO + H_2O$ and $Zn(OH)_2 = ZnO + H_2O$], oxides rather than hydroxides are formed as products.

The utility of the reactivity table (Table 3.3) in predicting what, if anything, will happen when a metal is added to an acid, cold water, hot water, or the solution of a salt of another metal has been illustrated in the preceding paragraphs. Its use in predicting what will happen when the oxides of the metals are heated or added to water and the metals themselves are heated in air or in oxygen has already been discussed in Sections 3.15, 3.16, 3.18, and 3.20. Additional uses will be brought out later (see the chart opposite inside back cover), all emphasizing the fact that, even though it gives no exact quantitative information, it still is an extremely useful and valuable table. Time spent in mastering the use of the table is very much worth while.

4.7 Oxidation-reduction in replacement reactions. When zinc reacts with H_2SO_4 according to the equation

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

the oxidation number of zinc increases from 0 in Zn to +2 in $ZnSO_4$. Therefore the zinc is oxidized. The oxidation number of hydrogen decreases from +1 in H_2SO_4 to 0 in H_2. Therefore hydrogen is reduced. The reaction is therefore an oxidation-reduction reaction in which zinc is the reducing agent and H_2SO_4 is the oxidizing agent. Likewise, the reaction

$$Zn + CuSO_4 = ZnSO_4 + Cu$$

is an oxidation-reduction reaction in which zinc is oxidized from an oxidation state of 0 in Zn to +2 in $ZnSO_4$, and copper is reduced from an oxidation number of +2 in $CuSO_4$ to 0 in Cu. Zinc is the reducing agent and $CuSO_4$ is the oxidizing agent. In the reaction

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2$$

Na is the reducing agent and H_2O is the oxidizing agent. Sodium is oxidized from an oxidation number of 0 in Na to +1 in NaOH, while hydrogen is reduced from +1 in H_2O to 0 in H_2.

When zinc reacts with steam,

$$Zn + H_2O = ZnO + H_2$$

the zinc is oxidized and the hydrogen is reduced, Zn being the reducing agent and H_2O the oxidizing agent.

4.8 Equilibrium in the reaction of a metal with steam. We have learned that when a metal such as zinc is heated in contact with steam, the reaction

$$Zn + H_2O + \text{heat} = ZnO + H_2$$

takes place.

When hydrogen gas is passed over an oxide such as ZnO at very high temperatures the reaction

$$H_2 + ZnO = Zn + H_2O$$

takes place.

It must follow, therefore, that if a mixture of Zn and H_2O is placed in a *closed container* and heated to a high temperature, both reactions will take place. Eventually the *rate* at which zinc reacts with steam to form ZnO and H_2 will be the same as the *rate* at which the hydrogen reacts with the zinc oxide to form Zn and H_2O. We will then have a *state of equilibrium* between four reactants. The reaction will keep on going round and round as long as the high temperature is maintained and the container is kept closed. The state of equilibrium can be indicated by using double arrows instead of the equality sign when writing the equation for the reaction.

$$Zn + H_2O \rightleftarrows ZnO + H_2$$

A detailed discussion of equilibrium in chemical reactions will be given in Chapter 10.

4.9 Commercial preparation of hydrogen. About $1\frac{1}{2}$ billion cubic feet of hydrogen gas (STP) are prepared in the United States each year. The methods used, in the approximate order of the amount of hydrogen produced by each, are:

1. *Catalytic reaction of steam with natural gas* (mostly methane, CH_4, and ethane, C_2H_6).

$$2\,H_2O + CH_4 + \text{heat and catalyst} = CO_2 + 4\,H_2$$

A number of different contact catalysts are used. The CO_2 is removed by washing with water.

$$CO_2 + H_2O = H_2CO_3$$

2. *Thermal decomposition (cracking) of natural gas*

$$CH_4 + \text{heat} = C + 2\,H_2$$
$$G_2H_6 + \text{heat} = 2\,C + 3\,H_2$$

3. *The catalytic reaction of steam with carbon (coke)*

$$C + 2\,H_2O + \text{heat and catalyst} = CO_2 + 2\,H_2$$

The CO_2 is removed by washing with water.

4. *Electrolysis of water*

$$2\,H_2O + \text{electric current} = 2\,H_2 + O_2$$

This method is important because it yields pure hydrogen and pure oxygen in one operation.

4.10 Commercial uses of hydrogen. The more important commercial uses of hydrogen, in the approximate order of amount of hydrogen consumed, are:

1. *Manufacture of ammonia*

$$N_2 + 3\,H_2 + \text{heat} + \text{pressure} + \text{catalyst} = 2\,NH_3$$

This process will be discussed in Chapter 18.

2. *Hydrogenation of vegetable and animal oil* to produce lard substitutes and "shortening" materials (see 4.4D).

3. *Manufacture of various organic chemical compounds* such as methyl alcohol.

$$CO + 2\,H_2 + \text{heat} + \text{pressure} + \text{catalyst} = CH_3OH$$

Increasing amounts of hydrogen are being used every year in the synthesis of an increasing number of compounds.

4. *Hydrogenation of coal* to produce a mixture of hydrocarbons which may be used as fuels, lubricating oil, and the like. As our supplies of petroleum decrease, hydrogenation of coal will become increasingly important as a source of fuel for power plants and internal combustion engines.

5. *For prevention of oxidation* in industrial metal-working furnaces. Not only does the hydrogen combine with any oxygen that might enter the furnace, thereby preventing it from oxidizing the metal, but it reduces to free metal any oxide on the surface of the metal.

6. *Welding and heating with the oxyhydrogen flame.* For certain purposes the carbon-free oxyhydrogen flame is more desirable than the oxyacetylene flame even though it is not so hot (about 2500°C maximum as compared with 3500°C).

4.11 Deuterium and tritium. There are 3 hydrogen isotopes; those with mass numbers of 2 and 3 are called *deuterium* (D) and *tritium* (T), respectively. The hydrogen found in nature in the form of water, cellulose, and other compounds consists of 99.98 parts by weight of ordinary hydrogen (H) with mass number of 1 and 0.02 parts by weight of deuterium. Water compounded from deuterium (D_2O) is called *heavy water*.

Tritium does not occur in nature. It can be synthesized in a manner which will be discussed in Chapter 8.

4.12 The molar volume of a gas. Table 2.2 presented experimental data to support the conclusion that 1 gram-molecular weight (1 mole) of any gas occupies a volume of 22.4 l at STP, and that the weight in grams of 22.4 l of a gas at STP is its gram-molecular weight. We noted, in this table that the molecular weights of oxygen, hydrogen, nitrogen, fluorine, chlorine, bromine, and iodine were twice their atomic weights, and that, accordingly, their molecules were diatomic, as represented by the formulas O_2, H_2, N_2, F_2, Cl_2, Br_2, and I_2.

Now that we have become familiar with a number of chemical reactions we can go back and examine the experimental evidence and scientific reasoning which led to the recognition of the facts enumerated in Table 2.2.

The French scientist Gay-Lussac had noted, in about 1800, that when gases are involved in chemical reactions the volumes of the reacting gases are in the ratio of small whole numbers as illustrated by the following examples.

hydrogen	+	oxygen	=	steam		
2 volumes		1 volume		2 volumes		
nitrogen	+	oxygen	=	nitrogen oxide		
1 volume		1 volume		2 volumes		
nitrogen	+	hydrogen	=	ammonia		
1 volume		3 volumes		2 volumes		
hydrogen	+	chlorine	=	hydrogen chloride		
1 volume		1 volume		2 volumes		

At about the same time John Dalton, an English schoolteacher, proposed, as two of the concepts of his atomic theory, that (a) when two or more elements combine to form a compound their atoms join together to form molecules of the compound, and (b) in general, atoms combine in simple ratio, 1 atom of A with 1, 2, or 3 atoms of B.

In line with Dalton's concepts the Italian physicist Avogadro postulated that the reason gases react with each other in the simple

integer volume ratios observed by Gay-Lussac is that equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules. The specific number of molecules of oxygen in a certain volume of oxygen will react with an equal number of molecules in the same volume of nitrogen.

Avogadro's postulate led to the following conclusions: Since 2 volumes of nitrogen oxide are formed from 1 volume of oxygen and 1 volume of nitrogen, these 2 volumes will contain twice as many molecules as were present in the 1 volume of oxygen or 1 volume of nitrogen. That means that 1 molecule of oxygen and 1 molecule of nitrogen combine to form 2 molecules of nitrogen oxide. Since a molecule of nitrogen oxide can contain no less than 1 atom of oxygen and 1 atom of nitrogen, a molecule of oxygen must contain at least 2 atoms of oxygen, and a molecule of nitrogen must contain at least 2 atoms of nitrogen. Likewise, since 1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrogen chloride, a molecule of hydrogen must contain at least 2 atoms of hydrogen, and a molecule of chlorine must contain at least 2 atoms of chlorine. Since there is no known reaction in which 1 volume of oxygen, nitrogen, hydrogen, or chlorine yields more than 2 volumes of another gas, we can conclude that 1 molecule of oxygen, nitrogen, hydrogen, and chlorine each contains 2 atoms of the element; their formulas are therefore O_2, N_2, H_2, and Cl_2. Similar experimental evidence leads to the conclusion that the formulas of the fluorine, bromine, and iodine molecules are F_2, Br_2, and I_2, respectively.

Since 2 volumes of hydrogen gas react with 1 volume of oxygen gas to form 2 volumes of steam, a molecule of steam must contain 2 atoms of hydrogen and 1 atom of oxygen; and since 1 volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia, a molecule of ammonia must contain 1 atom of nitrogen and 3 atoms of hydrogen.

Since the formulas of oxygen, hydrogen, nitrogen, and chlorine are O_2, H_2, N_2, and Cl_2, respectively, their molecular weights are 32.00, 2.016, 28.00, and 70.93, respectively. Because 32.00 g of oxygen, 2.016 g of hydrogen, 28.00 g of nitrogen, and 70.93 g of chlorine each occupy a volume of 22.4 l at STP, it can be concluded that *the weight in grams of 22.4 l of any gas at STP is its gram-molecular weight.* The fact that 22.4 l of nitrogen oxide, measured at STP, weighs 30 g is in line with this conclusion and establishes the fact that the formula for a molecule of nitrogen oxide is NO. All the data given in Table 2.2 lend further support to the above conclusion.

Questions and Problems

1. Define or describe, and illustrate: reduction; reducing agent; oxidation-reduction reaction; redox reaction; hydrogenation; halogens; halides; acid; replacement reaction; thermal decomposition; cracking of a compound.

2. How would you distinguish between three colorless gases: air, oxygen, and hydrogen?

3. Enumerate the important chemical properties of hydrogen and illustrate each with two specific reactions.

4. Point out how the reactivity table, giving the order of reactivity of the metals, is of value in the study of the chemical behavior of these metals.

5. List the important laboratory sources of hydrogen. Give balanced illustrative equations to show its preparation from each source.

6. Give the equations for three important commercial methods for preparing hydrogen.

7. List the most important commercial uses of hydrogen.

8. Describe in detail how hydrogen gas is prepared and collected in the laboratory. Point out the precautions that must be taken and indicate why they are taken.

9. When a piece of zinc is dropped into some sulfuric acid containing a few drops of $CuSO_4$ solution, the rate of evolution of H_2 is more rapid than when a piece of zinc is dropped into pure sulfuric acid. Explain.

10. How could you demonstrate:
    (a) That zinc is a more active metal than copper?
    (b) That NiO is a more stable compound than CuO?
    (c) That MgO has a higher heat of formation than HgO?
    (d) That Ag_2O is a more active oxidizing agent than PbO?
    (e) That silver will catalyze the reaction of Zn with H_2SO_4?
    (f) That hydrogen is a reducing agent?
    (g) That the formula for a molecule of hydrogen gas is H_2?

11. Write balanced chemical equations for the following reactions:
    (a) zinc + sulfuric acid
    (b) sodium + cold water
    (c) zinc + steam (heated)
    (d) lead oxide + hydrogen (heated)
    (e) magnesium + silver nitrate solution

(f) hydrogen + fluorine (heated)
(g) coke + steam + catalyst + heat
(h) aluminum + hydrochloric acid
(i) calcium + cold water

12. How could you distinguish between each substance in the following pairs?

(a) CuO and MnO, black solids
(b) $HgCl_2$ and $MgCl_2$, colorless solutions
(c) Mg and Sn, metals
(d) Water and dilute HCl
(e) Solutions of NaOH and H_2SO_4
(f) Ca and Zn, metals

13. For the reaction $SiH_4 + 2\,O_2 = SiO_2 + 2\,H_2O$, point out: (a) the element oxidized, (b) the element reduced, (c) the initial and final oxidation number of the element oxidized, (d) the initial and final oxidation number of the element reduced, (e) the oxidizing agent, (f) the reducing agent, (g) the total change of oxidation number of the atoms of the element oxidized, (h) the total change of oxidation number of the atoms of the element reduced.

14. How will the rates of diffusion of H_2 and Cl_2 gases compare?

15. Calculate the per cent of hydrogen in C_2H_6.

16. Calculate the weight in grams of 12 l of dry hydrogen gas measured at 21°C and 744 mm.

17. How many grams of combined hydrogen are there in 20 l of C_2H_6 gas measured at −40°C and 780 mm?

18. A mixture of 4 g of hydrogen gas and 8 g of CH_4 gas were placed in a container under a pressure of 750 mm of mercury. Calculate the partial pressure of each of the two gases in the mixture.

CHAPTER 5

Some Calculations Based on Chemical Equations

Note to instructor: The chemical equations used to illustrate the solution of weight-weight, weight-volume, and volume-volume problems (Sections 5.1, 5.2, and 5.3) are all taken from the chapter on oxygen, Chapter 3. Therefore these problems can, if desired, be taken up in connection with or at the conclusion of the discussion of oxygen.

5.1 Calculation of weight-weight relationships from chemical equations. As already stated, a balanced chemical equation tells the exact *ratio* of the number of moles of reactants and products involved in a reaction. Thus the balanced equation

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O$$

tells us that when methane gas (CH_4) is burned in oxygen, CO_2 and H_2O are formed as products. The oxygen reacts with the CH_4 in the ratio of 2 moles of O_2 to 1 mole of CH_4, and the CO_2 and $2\,H_2O$ are formed in the ratio of 1 mole of CO_2 and 2 moles of H_2O to 1 mole of CH_4 burned. A mole is a definite quantity of a substance; this definite quantity can be expressed in units of grams per mole or, if the substance is a gas, liters per mole at STP.

It follows therefore that the balanced equation can be used as the basis for calculating how many grams or pounds or tons of one substance will be required to react with or can be prepared from a specific number of grams or pounds or tons of another substance. To illustrate, suppose we calculate the problem, How many grams of CO_2 gas will be formed by the complete combustion of 50.0 grams of CH_4 gas? We will proceed by the following steps.

1. *Write the balanced equation for the reaction*

$$CH_4 + 2\,O_2 = CO_2 + 2\,H_2O$$

2. *Designate, as in boldface type, the formulas* of the compounds with which the problem is concerned, the quantities of each, and the units in which the quantities are expressed.

$$\begin{array}{lll} & 50.0\text{ g} & X\text{ g} \\ \mathbf{CH_4} + 2\,O_2 = & \mathbf{CO_2} + & 2\,H_2O \end{array}$$

3. *Designate the number of moles* of each substance concerned and express the value of these moles in the desired units.

$$\begin{array}{lll} & 50.0\text{ g} & X\text{ g} \\ \mathbf{CH_4} + 2\,O_2 = & \mathbf{CO_2} + & 2\,H_2O \\ & 1\text{ mole} & 1\text{ mole} \\ & 16.0\text{ g} & 44.0\text{ g} \end{array}$$

4. *Solve for the quantity sought.* The equation tells us that 1 mole, or 16 g, of CH_4, when burned, will yield 1 mole, or 44 g, of CO_2. We can then solve for the number of grams of CO_2 that will be produced from 50 g of CH_4 either by the mole method, factor method, or by proportion.

By the mole method. The equation for the reaction tells us that 1 mole of CH_4 yields 1 mole of CO_2. Since the molecular weight of CH_4 is 16.0, 50.0 g of CH_4 is 50.0/16.0 moles. Therefore 50.0/16.0 moles of CO_2 will be produced. Since 1 mole of CO_2 weighs 44.0 g the 50.0/16.0 moles will weigh

$$\frac{50.0}{16.0} \times 44.0, \text{ or } 137\text{ g}$$

Expressed in one operation the solution is

$$\frac{50.0}{16.0}\text{ moles} \times 44.0\text{ g of } CO_2/\text{mole} = 137\text{ g of } CO_2$$

By the factor method. Our thinking, in the factor method, is that we start with 50.0 g of CH_4 and we want to know into how many grams of CO_2 this CH_4 can be *converted.* To *convert* grams of CH_4 to grams of CO_2 we must multiply by the *factor* "grams of CO_2 per gram of CH_4." If we do this "grams of CH_4" in the numerator will cancel "grams of CH_4" in the denominator. The answer, as noted in the equation below, will be "grams of CO_2."

$$\text{grams of } CH_4 \times \frac{\text{grams of } CO_2}{\text{grams of } CH_4} = \text{grams of } CO_2$$

The factor, "grams of CO_2 per gram of CH_4," will, we observe from the balanced equation, be 44 g of CO_2/16 g of CH_4. Therefore our factor solution will be

$$50.0\text{ g of } CH_4 \times \frac{44.0\text{ g of } CO_2}{16.0\text{ g of } CH_4} = 137\text{ g of } CO_2$$

By proportion. Our thinking, in proportion, runs like this: Since 44 g of CO_2 are produced from 16 g of CH_4, then X g of CO_2 will be produced from 50 g of CH_4. Expressing this proportion in fractional

form we have

$$\frac{44.0 \text{ g of } CO_2}{16.0 \text{ g of } CH_4} = \frac{X \text{ g of } CO_2}{50.0 \text{ g of } CH_4}$$

Solving by transposition we get

$$X \text{ g of } CO_2 = 50.0 \text{ g of } CH_4 \times \frac{44.0 \text{ g of } CO_2}{16.0 \text{ g of } CH_4}$$
$$= 137 \text{ g of } CO_2$$

Note that the final equation in the proportion method is the one equation in the factor method. The factor method is just a shortened form of the proportion method.

Suppose the problem had read, How many *pounds* of CO_2 gas will be formed by the complete combustion of 50.0 *pounds* of CH_4 gas?

We would proceed exactly as in the previous solution except that we would note that the equation

$$\underset{\substack{1 \text{ mole} \\ 16 \text{ g}}}{CH_4} + 2\,O_2 = \underset{\substack{1 \text{ mole} \\ 44 \text{ g}}}{CO_2} + 2\,H_2O$$

tells us that the CH_4 that is burned and the CO_2 that is formed are in the ratio of *16 parts by weight* of CH_4 to *44 parts by weight* of CO_2. That means that 16 lb of CH_4 will yield 44 lb of CO_2, and the factor, giving the ratio of the weight of the CO_2 to the weight of the CH_4 will be 44/16. The solution, by the mole method, will be

$$\frac{50}{16} \text{ moles} \times 44 \text{ lb of } CO_2/\text{mole} = 137 \text{ lb of } CO_2$$

Solution by the factor method will be

$$50 \text{ lb of } CH_4 \times \frac{44 \text{ lb of } CO_2}{16 \text{ lb of } CH_4} = 137 \text{ lb of } CO_2$$

and by proportion, will be

$$\frac{44 \text{ lb of } CO_2}{16 \text{ lb of } CH_4} = \frac{X \text{ lb of } CO_2}{50 \text{ lb of } CH_4}$$

$$X = 50 \text{ lb of } CH_4 \times \frac{44 \text{ lb of } CO_2}{16 \text{ lb of } CH_4} = 137 \text{ lb of } CO_2$$

If the weight were expressed in tons the solution would be the same as for grams or pounds. The balanced equation gives the *ratio* in parts by weight of one substance to parts by weight of another; it makes no difference in solving the problem what weight units are used.

5.2 Calculation of weight-volume relationships from chemical equations. Suppose we are asked to solve the problem, How many

grams of CO_2 gas will be formed by complete combustion of 50 *liters* of CH_4 gas measured at STP? We proceed exactly as in the weight-weight calculation except that the units are now 50 l of CH_4 and X g of CO_2. Since 1 mole of any gas occupies a volume of 22.4 l at STP, step 3 will then have this setup:

$$\begin{array}{lll} & 50.0\ \text{l} & X\ \text{g} \\ \text{CH}_4 + 2\,\text{O}_2 & = & \text{CO}_2 + 2\,\text{H}_2\text{O} \\ & 1\ \text{mole} & 1\ \text{mole} \\ & 22.4\ \text{l} & 44.0\ \text{g} \end{array}$$

Solving by the mole method, we find that there are 50.0/22.4 moles of CH_4. Therefore 50.0/22.4 moles of CO_2 will be formed.

$$\frac{50.0}{22.4}\ \text{moles} \times 44.0\ \text{g of CO}_2\text{/mole} = 98.1\ \text{g of CO}_2$$

The factor solution will be

$$50.0\ \text{l of CH}_4 \times \frac{44.0\ \text{g of CO}_2}{22.4\ \text{l of CH}_4} = 98.1\ \text{g of CO}_2$$

and the proportion will be

$$\frac{44.0\ \text{g of CO}_2}{22.4\ \text{l of CH}_4} = \frac{X\ \text{g of CO}_2}{50.0\ \text{l of CH}_4}$$

If conditions are not standard, the volume of the gas must be converted to STP by the use of the gas law equation ($PV = nRT$, or, $V_1P_1/T_1 = V_2P_2/T_2$).

5.3 Gay Lussac's law of combining volumes. Calculation of volume-volume relationship of gases from chemical equations. Hydrogen and oxygen are formed in the ratio of 2 moles of hydrogen gas to 1 mole of oxygen when water is electrolyzed. Since 1 mole of one gas will, at the same temperature and pressure, occupy the same volume as 1 mole of any other gas, the volume of the hydrogen gas will be twice as great as the volume of the oxygen gas. This simple integer ratio between the volumes of the gases involved illustrates Gay Lussac's law of combining volumes, which states that *in any reaction in which two or more gases are involved, the volumes of the gases at the same temperature and pressure are to each other as the small whole numbers representing the number of moles.*

$$\begin{array}{lll} 2\,\text{H}_2\text{O} & = & 2\,\text{H}_2 + \text{O}_2 \\ & & 2\ \text{moles}\quad 1\ \text{mole} \\ & & 2\ \text{volumes}\quad 1\ \text{volume} \end{array}$$

The burning of methane gas to form CO_2 gas and steam (H_2O) also illustrates the law.

$$\underset{\substack{1\text{ mole}\\1\text{ volume}}}{CH_4} + \underset{\substack{2\text{ moles}\\2\text{ volumes}}}{2\,O_2} = \underset{\substack{1\text{ mole}\\1\text{ volume}}}{CO_2} + \underset{\substack{2\text{ moles}\\2\text{ volumes}}}{2\,H_2O}$$

The volumes of all gases must of course be measured at the same temperature and pressure.

Suppose we are asked to solve the problem, How many liters of CO_2 gas will be formed by burning 50 l of CH_4 gas? Both gases are measured at the same temperature and pressure. We will proceed as with the two preceding types of problems (Sections 5.1 and 5.2). Step 3 will then yield

$$\begin{array}{ll} 50\text{ l} & X\text{ l} \\ CH_4 + 2\,O_2 = & CO_2 + 2\,H_2O \\ \text{1 mole} & \text{1 mole} \\ \text{22.4 l} & \text{22.4 l} \\ \text{1 volume} & \text{1 volume} \end{array}$$

We note that the volume of the 1 mole of CH_4 (22.4 l) is the same as the volume of the 1 mole of CO_2 (22.4 l), so we apply Gay-Lussac's law of combining volumes and note, by mental calculations, that the answer is 50 l of CO_2, the same volume as that of the CH_4 gas that we started with.

5.4 Equivalent weight. In the language of chemistry, *two quantities of substances are equivalent to each other when they will react with each other or replace each other.* Thus the formula KH for potassium hydride and the equation

$$2\,K + 2\,HCl = 2\,KCl + H_2$$

both tell us that 1 gram-atom of potassium is equivalent to 1 gram-atom of hydrogen. Likewise, from the formulas NaH, LiH, RbH, and CsH and the reactions

$$\begin{aligned} 2\,Na + 2\,HCl &= 2\,NaCl + H_2 \\ 2\,Li + 2\,HCl &= 2\,LiCl + H_2 \\ 2\,Rb + 2\,HCl &= 2\,RbCl + H_2 \\ 2\,Cs + 2\,HCl &= 2\,CsCl + H_2 \end{aligned}$$

we see that 1 gram-atom of sodium, lithium, rubidium, or cesium is each equivalent to 1 gram-atom of hydrogen.

The formulas HF, HCl, HBr, and HI show that 1 gram-atom of fluorine, chlorine, bromine, or iodine is each equivalent to 1 gram-atom of hydrogen.

Quantities of two chemical substances that are each equivalent to the same thing are equivalent to each other. Thus, since 1 gram-atom of sodium and 1 gram-atom of chlorine are each equivalent to 1 gram-atom of hydrogen (NaH, HCl) they should then be equivalent to each other; the formula NaCl shows that this is true.

The formula CaH_2 and the equation

$$Ca + 2\,HCl = CaCl_2 + H_2$$

show that 1 gram-atom of calcium is equivalent to 2 gram-atoms of hydrogen, and the formula $CaCl_2$ shows that 1 gram-atom of calcium is equivalent to 2 gram-atoms of chlorine. That means that $\frac{1}{2}$ gram-atom of calcium is equivalent to 1 gram-atom of hydrogen and also to 1 gram-atom of chlorine. The equation

$$2\,Al + 6\,HCl = 2\,AlCl_3 + 3\,H_2$$

shows that 1 gram-atom of aluminum is equivalent to 3 gram-atoms of hydrogen, and the formula $AlCl_3$ shows that 1 gram-atom of aluminum is equivalent to 3 gram-atoms of chlorine. One-third gram-atom of aluminum is therefore equivalent to 1 gram-atom of hydrogen and also to 1 gram-atom of chlorine.

The formula H_2O tells us that 1 gram-atom of oxygen is equivalent to 2 gram-atoms of hydrogen. One-half gram-atom of oxygen and 1 gram-atom of hydrogen are therefore equivalent to each other.

Since 1 gram-atom of hydrogen, 1 gram-atom of chlorine, and $\frac{1}{2}$ gram-atom of oxygen are equivalent to each other, we can use each of these quantities as standards of reference. We can then define the *equivalent weight* of an element as that weight which will combine with or replace 1 gram-atom (1.008 g) of hydrogen, 1 gram-atom (35.46 g) of chlorine, or $\frac{1}{2}$ gram atom (8.00 g) of oxygen. Since the unit in which equivalent weight is expressed will, on the basis of the above definition, be in grams, it is customary to speak of it as *gram-equivalent weight.*

The equivalent weight can be calculated from the experimentally determined chemical formulas. Thus, since the formula of methane is CH_4, the equivalent weight of carbon is one-quarter its gram-atomic weight. Likewise, the equivalent weight of silicon in SiO_2 is one-quarter its gram-atomic weight. The equivalent weight of nitrogen in NH_3 is one-third its gram-atomic weight, and the equivalent weight of nitrogen in NO is one-half its gram-atomic weight. We can see from these values that *the gram-equivalent weight of an element in its binary compounds is its gram-atomic weight divided by its valence (oxidation number).* The equivalent weight of an element will therefore vary with its oxidation number.

By the term *equivalent quantities* of two substances is meant the quantities that will react with each other or with some standard equivalent quantities. The concept of equivalent weights enables us to calculate equivalent quantities because a certain fraction of an equivalent weight of one element will always unite with the same fraction of an equivalent weight of any other substance. Thus one-tenth equivalent weight of Al will combine with one-tenth equivalent weight of Cl, and one one-thousandth equivalent weight of Mg will combine with one one-thousandth equivalent weight of bromine.

It should be noted here that the concept of equivalent weight can be applied to compounds as well as elements, equivalent quantities of two compounds being the quantities that will react with each other. Equivalence in compounds will be discussed in detail in later chapters.

Problems

1. How many moles of CO_2 and how many moles of H_2O will be formed by complete combustion in oxygen of 5 moles of C_6H_6?

2. How many moles of oxygen gas will be formed by complete decomposition of 10 moles of H_2O?

3. How many moles of CO_2 will be formed by complete combustion of 0.2 mole of CH_4?

4. How many moles of CO_2 will be formed by complete combustion of 120 g of C_2H_6?

5. How many gram-atoms of carbon must be burned to yield 0.3 mole of CO_2?

6. How many grams of oxygen gas can be obtained by heating 160 g of pure $KClO_3$?

7. How many grams of pure HgO would have to be heated in order to obtain 80 g of pure oxygen? What volume would these 80 g of pure dry oxygen gas occupy at STP?

8. How many liters of CO_2 gas, measured at STP, will be formed by complete combustion of 120 g of $C_6H_{10}O_5$?

9. How many liters of oxygen gas will be required for complete combustion of 150 l of C_2H_4 gas, and how many liters of CO_2 gas will be formed? All gases are measured at the same temperature and pressure.

10. A compound containing 63.3% manganese and 36.7% oxygen was heated until no more reaction took place, oxygen gas having been evolved. The solid product was a compound containing 72% man-

ganese and 28% oxygen. Write the balanced equation for the reaction that took place.

11. How many moles of hydrogen gas will be required for the formation of 24 moles NH_3?

12. How many grams of hydrogen gas will be liberated from an excess of sulfuric acid by 125 g of aluminum?

13. How many grams of magnesium must be treated with an excess of hydrochloric acid in order that 4.0 g of hydrogen gas shall be liberated?

14. How many liters of hydrogen gas measured at STP will be required for the reduction of 25 g of CuO?

15. How many liters of hydrogen gas must be combined with nitrogen gas to yield 60 l of NH_3 gas? All gas volumes are measured at the same temperature and pressure.

16. Hydrogen gas was passed over a solid compound which contained 36.5% K, 33.3% Cl, and 30.2% O. When the reaction was complete there remained a solid compound which contained 53% K and 47% Cl. Write the balanced equation for the chemical reaction which took place.

17. What is the equivalent weight of the element set in boldface in each of the following compounds? $\mathbf{Fe}_2O_3$; $\mathbf{Fe}O$; $\mathbf{N}_2O$; $\mathbf{P}H_3$; $\mathbf{Cr}Cl_3$; $\mathbf{N}_2O_5$; $\mathbf{Sn}O_2$; $\mathbf{Cu}Cl_2$; $H_2\mathbf{S}$; $\mathbf{S}O_2$.

18. When 3.04 g of a metal were burned in oxygen, 5.04 g of oxide were formed. Calculate the equivalent weight of the metal.

19. When treated with HCl, 1.0 g of a metal liberated 381 cc of hydrogen gas collected and measured over water at 20°C and 737.4 mm. Calculate the equivalent weight of the metal.

CHAPTER 6

The Periodic Table

6.1 Evidence that selected groups of elements have similar properties. In the detailed study of oxygen and hydrogen in Chapters 3 and 4, a large number of specific facts about each of these two elements were listed. One naturally wonders whether, in the study of chemistry, it is going to be necessary to make the same sort of detailed enumeration of specific facts for each of the remaining 98 elements. Is it not possible to arrange the 100 elements in some manner so that those with similar properties fall together in small groups? If such an arrangement could be made, much enumeration and memorization of specific facts about each element could be avoided and the study of chemistry would be greatly simplified. That there is a similarity between groups of elements and that variations in degree of similarity may be related in some way to the atomic weights of the elements is indicated by the following facts which have been noted in our study up to this point.

✓ 1. *The reactive elements may be divided into two major categories, metals and nonmetals.* The following differences between metals and nonmetals have been noted:

(a) The metals, all except one of which are solids at room temperature, acquire a high luster when polished; this is commonly referred to as metallic luster. Most nonmetals are gases or liquids at room temperature; the solid nonmetals do not acquire a luster when polished.

(b) The metals are good conductors of heat and electricity, the nonmetals are poor conductors.

(c) The oxides of metals are, as a general rule, solids with relatively high melting points (see Table 3.5). The oxides of nonmetals are either gases, liquids, or low-melting solids (see Table 3.6).

(d) The metals can be arranged in a table representing their order of reactivity, hydrogen being included for reference (see Table 3.3). A similar reactivity table can be drawn up for the nonmetals (see Table 3.4).

(e) The oxides of reactive nonmetals react with water to form acids. The oxides of reactive metals react with water to form hydroxides; solutions of these hydroxides are bases. In other words, nonmetals are acid-forming elements, while metals are base-forming.

(f) The metals that are more reactive than hydrogen displace hy-

drogen from acids, salts being formed as products. Nonmetals do not displace hydrogen from acids.

(g) The most reactive metals displace hydrogen from cold water, hydroxides being formed as products. The other metals above hydrogen displace hydrogen from steam at high temperatures, oxides being formed as products. None of the nonmetals liberates hydrogen from cold water, and only one (carbon) liberates it from steam at high temperatures.

(h) The nonmetals all form stable binary hydrogen compounds. These compounds are all gases with the exception of H_2O, which is a liquid. As a general rule only the most reactive metals form stable hydrides; the few metal hydrides about which data are available are solids with moderately high melting points.

2. *Helium, neon, argon, krypton, xenon, and radon are similar.*

(a) They are all colorless, odorless, tasteless gases.

(b) They are all monatomic. All other elementary gases are diatomic.

(c) They are chemically inert. They do not react with any other elements. All other elements are reactive.

3. *The metals lithium, sodium, potassium, rubidium, and cesium are similar.*

(a) All five react rapidly with cold water to liberate hydrogen and form the hydroxide of the metal.

(b) All five react violently with hydrochloric acid to liberate hydrogen and form the chloride of the metal.

(c) All five react rapidly with oxygen to form solid oxides. The heats of formation of these oxides are all very high, and their melting points are moderately high (see Table 3.5).

(d) They all combine directly with hydrogen at moderately high temperatures to form stable hydrides.

(e) They all have oxidation numbers of +1 in all their compounds.

(f) Their hydroxides are all very soluble in water.

(g) The solutions of their hydroxides all react strongly basic toward litmus paper.

(h) Their solid binary compounds are all white. Water solutions of these compounds are all colorless.

4. *The metals barium, strontium, calcium, magnesium, and beryllium are similar.*

(a) They all have oxidation numbers of +2 in all their compounds.

(b) Their oxides are all white solids with high melting points and high heats of formation (see Table 3.5).

(c) Barium, strontium, and calcium react with cold water to liberate

hydrogen and form the hydroxide; the rate of reaction decreases as the atomic weight decreases. Beryllium and magnesium do not react with cold water but do react slowly with steam.

(d) The solubility of their hydroxides in water decreases as the atomic weight of the metal decreases, $Ba(OH)_2$ being moderately soluble and $Be(OH)_2$ only slightly soluble.

(e) The solutions of their hydroxides react basic to litmus paper.

(f) Barium, strontium, and calcium react directly with heated hydrogen to form stable hydrides; Mg and Be do not react with hydrogen.

(g) They all react with acids such as HCl, the rate of the reaction decreasing as the atomic weight of the metal decreases.

5. *The nonmetals fluorine, chlorine, bromine, and iodine are similar.*

(a) Their binary hydrogen compounds:

i. All have the same general formula, HF, HCl, HBr, HI, in which the oxidation number of the halogen is -1.

ii. All are colorless gases.

iii. All have similar sharp, irritating odors.

iv. All fume strongly in moist air.

v. Decrease in stability toward heat as the atomic weight of the halogen increases.

vi. All are very soluble in water. The solutions all react strongly acidic to litmus paper.

vii. Have decreasing heats of formation as the atomic weight of the halogen increases.

(b) The reactivity of the halogen decreases markedly as its atomic weight increases (see Table 3.4).

(c) As the atomic weight of the halogen increases, there is a regular increase in the depth of the color of the element and a regular increase in the density. Fluorine is a pale yellow gas whose density is 38 g/22.4 l. Greenish-yellow chlorine gas has a density of 71 g/22.4 l. Bromine is a reddish-brown liquid, while iodine is a black solid.

6. *There is distinct similarity between the nonmetals oxygen, sulfur, selenium, and tellurium.*

(a) Their binary hydrogen compounds have similar formulas, H_2O, H_2S, H_2Se, and H_2Te. The oxidation number of the nonmetal is -2 in each case.

(b) H_2S, H_2Se, and H_2Te are all gases with foul odors.

(c) The solutions of H_2S, H_2Se, and H_2Te in water are acidic.

(d) The heat of formation of the binary hydrogen compound decreases as the atomic weight of the nonmetal increases.

(e) They all combine with metals to form oxides, sulfides, selenides,

and tellurides with the same general formula (MgO, MgS, MgSe, MgTe).

(f) There is an increase in density of the element with increase in atomic weight.

7. *The elements nitrogen, phosphorus, arsenic, and antimony are similar.*

(a) They form analogous hydrogen compounds, NH_3, PH_3, AsH_3, and SbH_3, all of which are gases with similar odors. Their oxidation numbers in these compounds are all -3.

(b) They form analogous oxides: N_2O_5, P_4O_{10}, As_2O_5, and Sb_2O_5, in which their oxidation numbers are $+5$; and N_2O_3, P_2O_3, As_2O_3, and Sb_2O_3, in which their oxidation numbers are $+3$.

(c) There is an increase in density of the elements with increase in atomic weight.

8. *The nonmetals carbon and silicon are similar.*

(a) Both form gaseous hydrogen compounds, CH_4 and SiH_4, in which their oxidation numbers are -4.

(b) Both form analogous oxides CO, CO_2, SiO, and SiO_2 in which their oxidation numbers are $+2$ and $+4$.

9. *There is some similarity between boron and aluminum.* Both form white, solid oxides, B_2O_3 and Al_2O_3, in which their oxidation numbers are $+3$.

The cases cited above indicate, beyond much question, that certain of the elements do fall into groups and that, within a group, there is distinct similarity of properties. The question now arises, Is there some systematic basis on which the grouping of the elements can be made? Is there some one property that will serve as a guide or key to the systematic grouping? To get the answer to these questions we must take note of an outstandingly significant property of the 100 elements, *the atomic number.*

6.2 The atomic number of an element. When a stream of electrons originating at the negative pole in an x-ray tube (see Figure 6.1) falls upon the pure target element that constitutes the positive pole, the atoms of the target element give off x rays. Each element when used as a target produces x rays of a definite wavelength. *As the atomic weight of the element increases, the wavelength of the x ray which it produces decreases.* The *order* of the wavelength of the x ray that is produced when the element is used as a target is called the *atomic number* of the element. Hydrogen, which has the smallest atomic weight is assigned an atomic number of 1. Proceeding from H to He to Li to Be to B to C and so on in the order of increasing atomic weights down the complete list of the 100 elements given in Table 6.1, the wavelengths of the x rays decrease

6.3 The atomic number and the periodic recurrence of elements with similar properties. If the elements in Table 6.1 are arranged in a horizontal row in the order of their increasing atomic numbers, starting with hydrogen on the left, the tenth element, the inert gas neon, is obviously similar to the second element, the inert gas helium. If neon is then placed under the element helium to start a new horizontal row, the arrangement, with the atomic numbers of each element, will look like this:

H	He	Li	Be	B	C	N	O	F
1	2	3	4	5	6	7	8	9
	Ne							
	10							

The next element is sodium, number 11. As has been pointed out in Section 6.1, sodium definitely is similar to lithium and belongs in the same group with it just as neon definitely is similar to and belongs in the same group with helium. As the placement process continues, element 12, magnesium, falls in with beryllium where, on the basis of what has been summarized in Section 6.1, it belongs. Element 13, aluminum, falls in with boron; the experimental evidence given in Section 6.1 is pretty sketchy but what little there is justifies placing boron and aluminum in the same group. It should be stated that more detailed information about boron and aluminum further justifies their being placed in the same group. As has been pointed out in Section 6.1, silicon (14), phosphorus (15), sulfur (16), and chlorine (17) are very similar to carbon, nitrogen, oxygen, and fluorine, respectively. The arrangement up to this point is:

H	He	Li	Be	B	C	N	O	F
1	2	3	4	5	6	7	8	9
	Ne	Na	Mg	Al	Si	P	S	Cl
	10	11	12	13	14	15	16	17

Leaving out hydrogen, the 16 elements listed definitely fall into 8 pairs of similar elements.

Element 18 is the inert gas argon, 19 is potassium, and 20 is calcium. There is no question, on the basis of what has been stated in Section 6.1, that A falls in with He and Ne, that K falls in with Li and Na, and that Ca falls in with Be and Mg. Element 21 is scandium. Here we run into trouble because the next eight elements, Sc, Ti, V, Cr, Mn, Fe, Co, and Ni do not fit in with Al, Si, P, S, Cl, A, K, and Mg the way the elements have been fitting up to this point. Not until we have unrolled ten elements and get to gallium, number 31, do we find an element that is

reasonably similar to aluminum. However, the next seven elements after gallium (Ge, As, Se, Br, Kr, Rb, and Sr) are very similar to the elements into whose groups they fall. If we string out the ten elements between calcium and gallium the arrangement, up to this point becomes:

H	He	Li	Be											B	C	N	O	F
1	2	3	4											5	6	7	8	9
	Ne	Na	Mg											Al	Si	P	S	Cl
	10	11	12											13	14	15	16	17
	A	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35
	Kr	Rb	Sr															
	36	37	38															

Another sequence of ten elements must be unrolled beyond strontium (38) before we find an element, indium (49), that is reasonably similar to B, Al, and Ga; but here again, as in the previous case, the next eight elements, Sn, Sb, Te, I, Xe, Cs, and Ba, definitely belong in the same groups with the elements into whose groups they fall. To our gratification we find that the sequence of ten elements, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, and Cd, falls into a logical grouping with the sequence of ten elements previously unrolled. This gives us, up to this point, an arrangement like that shown in the first five horizontal rows (periods) and a part of the sixth row of the periodic table on the inside back cover, except that in the table the vertical column containing He, Ne, A, Kr, and Xe has been placed at the extreme right.

Beyond Ba (56) we run into more trouble. The next element, La (57), is similar to Sc (21) and Y (39); but so are the next 14 elements! Not until we get to hafnium (Hf, 72) do we find an element similar to Zr. The 15 elements, La (57) to Lu (71) are called the *lanthanides* or *rare earth metals*. They are very similar to each other and all have oxidation number of +3.

Beyond hafnium (72) we get the logical arrangement shown in the periodic table on the inside back cover. It is interesting and significant that, just as barium (56) is followed by 14 lanthanides before the pattern of 10 elements set up in periods 4 and 5 is repeated, so in period 7 (horizontal row 7), radium (88) is followed by a group of elements all of which are similar to Sc, Y, and La. Presumably there should be another sequence of 15 elements corresponding to the lanthanides, but only 12 of them are known. This incomplete sequence is known as the *actinide* series.

The complete arrangement, known as the *long form of the periodic table*, is represented on the inside back cover.

It should be stated at this point that the arrangement of the elements given in the long form of the periodic table did not develop, full blown, in the simple fashion in which it has been described. Dobereiner first noted similarities between elements in 1829. Newlands noted, in 1863, that when the elements are arranged in the order of their increasing atomic weights, the eighth element, starting from a given one, repeats the properties of the first. Working independently, the German chemist Lothar Meyer and the Russian chemist Mendeleev both drew up, in 1869, periodic tables very similar to the one given in this book, and enunciated the law, called the *periodic law*, which stated that the properties of the elements are *periodic functions of their atomic weights.* Atomic numbers were not determined by Moseley until 1913. The modern periodic table is a product of the thought and labor of hundreds of scientists.

As noted above, the arrangement of the elements in the long form periodic table results from the fact that certain characteristic properties recur at regular intervals when these elements are arranged in the order of increasing atomic numbers. This means that the properties of the elements are *periodic functions of their atomic numbers.* This is the modern statement of the periodic law.

6.4 Structural features of the periodic table. The vertical columns are called *groups.* The horizontal rows are *periods.* Periods 1, 2, and 3 are referred to as *short periods;* periods 4, 5, and 6 are *long periods.* Period 7 is an *incomplete long period.* The significance of the number and accompanying letter (IA, IIIB) used to designate each group will be brought out in later discussion; at the moment they simply serve to identify the group.

6.5 Relation between the properties of an element and its position in the periodic table. A complete picture of the relationship between the properties of an element and its position in the periodic table cannot be presented until the theory of the structure of the atom has been developed in Chapter 7. Only those relationships which involve considerations already discussed will be brought out at this time.

A. *The inert gases fall in group* 0 *at the extreme right.*

B. *Hydrogen is unique and does not properly belong in any group with any other elements.*

C. *The strongly reactive metals, referred to as the alkali metals and the alkaline earth metals,* fall at the extreme left in groups IA and IIA; because of their low densities they are also referred to as the *light metals.*

The distinctly nonmetallic elements fall to the right and above the diagonal zigzag line in the right-hand side of the table in groups IIIA, IVA, VA, VIA, and VIIA. The elements near the left-hand side of the zigzag line are largely metallic but somewhat nonmetallic in their chemical and physical behavior; they are sometimes referred to as *metalloids*. The elements to the right of group IIA and to the left of group IIIA are the *transition metals*, so called because they represent a transition in character from the reactive metals on the left to the nonmetals on the right; they are also referred to as the *heavy metals* because of their high densities. It should be noted that there is some difference of opinion among scientists as to what metals should be included in the transition class and what the criteria for placement in this category should be.

D. *In general the elements in a group have similar properties.* Variations in the chemical properties of the elements in a group is a matter of degree and this variation is generally proportional to the change in atomic number. Variation in physical properties is, in many instances, also proportional to the change in atomic number. The complete significance of these statements will be brought out when the properties of the elements in the respective groups are studied in detail. They can, however, be illustrated by reference to what we have learned about some of the elements in Chapters 3 and 4. Thus Ba, Sr, Ca, Mg, and Be, in group IIA, are all fairly reactive metals with oxidation numbers of +2. Their reactivities, as shown by the rates at which they react with water and the rates at which they liberate hydrogen from hydrochloric acid, increase as their atomic numbers increase. The solubilities in water of their hydroxides increase as their atomic numbers increase. One would predict that radium, about which nothing was said in Chapters 3 and 4, would be the most reactive metal in group IIA, and its hydroxide would be the most soluble. Such, in fact, is the case. Not all properties of these elements vary directly with their atomic numbers. For example, the densities and melting points of the metals and the heats of formation of their oxides vary as indicated in Table 6.2. The densities are all low, the melting points are all fairly high, and the heats of formation are all

TABLE 6.2

PROPERTIES OF ALKALINE EARTH METALS

	Be	Mg	Ca	Sr	Ba	Ra
Atomic number.....	4	12	20	38	56	88
Density.....	1.8	1.74	1.55	2.6	3.5	5
Melting point, °C...	1,350	651	810	800	850	960
Heat of formation of oxide (cal/mole)..	146,000	143,840	151,900	141,100	133,400	125,000

very high, so in these respects they are all similar. There is, however, no direct relationship between these properties and the atomic numbers.

The similarities of the elements in group 0 (the inert gases), group IA (Li, Na, K, Rb, Cs), group VIIA (F, Cl, Br, I), group VIA (O, S, Se, Te), and group VA (N, P, As, Sb) have already been pointed out in Section 6.1.

We will find, as our study progresses, that the properties of the elements of an A group are more nearly similar than are those of B group elements. Likewise the variation of a property is more nearly proportional to the atomic number in the A groups than in the B groups.

In general, we should be warned that the periodic law is not so exact that we can learn the properties of one element in the group and then predict the properties of the other elements. The periodic law points the way and shows the trend, but cannot be counted on to supply the exact details. The value of the periodic table as a guide to systematic study of the properties of the elements and their compounds far outweighs any disadvantage which results from this inability to supply exact details. This will be brought out strongly as we proceed farther in this book. Not until all the elements have been studied can one fully appreciate just how valuable a tool the periodic table is.

CHAPTER 7

Atomic Structure

7.1 Experimental facts and the concept of atomic structure. A satisfactory concept of the detailed structures of the atoms of the 100 elements must account for or be consistent with a large number of experimental facts and concepts relating to these facts, among which are the following:

1. Atomic weights and the experimentally observed change in physical and chemical properties with change in atomic weight.

2. The existence of isotopes.

3. Atomic numbers. What structural feature of the atom accounts for the observed regularity of change of x-ray wavelength with increase in atomic weight? Why is the change in wavelength of the x ray completely uniform in going from one atom to the atom of next higher atomic weight whether the difference in atomic weight is small, as between Se and Br, or large, as between Cs and Ba? Why do the isotopes of an element yield x rays of the same wavelength even though their atomic weights are different?

4. The periodicity of the properties of the elements as represented by the periodic table. Why does this periodicity exist? Why is hydrogen unique and in a class by itself? Why does the periodicity result in there being 2 elements in the first period, 8 in the second, 8 in the third, 18 in the fourth, 18 in the fifth, and 32 in the sixth? How account for the sequences of 2 elements in the first period, 2 and 6 elements in periods two and three, 2, 10, and 6 elements in periods four and five, 2, 14, 10, and 6 elements in period six, and 2 and 12 elements in period seven?

5. The inertness of the gases He, Ne, A, Kr, and Xe.

6. The great chemical reactivity of the metals in groups IA and IIA.

7. The similarity in chemical behavior but the great difference in reactivity of F, Cl, Br, and I.

8. The increase in reactivity of the metals of group IIA with increase in atomic weight.

9. The difference in chemical properties between metals and nonmetals.

10. The concept of combining capacity, valence, or oxidation number.

11. The difference in conductivity, ductility (ability to be drawn into

fine wires), and malleability (ability to be pounded out into thin sheets) of metals and nonmetals.

12. The electric conductivity of some fluid compounds such as melted salts and the nonconductivity of other fluid compounds.

13. Radioactivity and transmutation of elements.

7.2 The constituent parts of the atom. The modern concept of the structure of the atom is the result of untold hours of thought, speculation, research, and experimentation by thousands of scientists all over the world. A great variety of scientific information has aided in the development of the concept, but the greatest contribution has come from study of the spectra of hydrogen and the other elements (the spectrum of an element is the light, invisible as well as visible, which the incandescent element emits or which the incandescent vapors of the element absorb). The mathematical equations and calculations which are called into play in the interpretation of these spectral data are too involved to be considered in a book of this scope. Accordingly, only the simple finished picture will be presented. Since the concepts of atomic structure are derived from the properties displayed by the elements and are intended to account for these properties, and since, as we have already seen, the periodic table represents a systematic arrangement of the elements on the basis of their properties, it follows that the structure of the atom of an element must be closely correlated with its position in the periodic table. This correlation will be the focal point in the discussion that follows. It must not be concluded from this discussion, however, that the scientists simply took the periodic table and built an atomic picture to coincide with it. The modern periodic table and the structure of the atom were developed concurrently; each contributed to the development of the other.

According to modern theory the atom is constructed like a miniature solar system. The nucleus, corresponding to the sun, is a small, dense mass made up of two kinds of particles, *neutrons* and *protons*. Revolving around this nucleus in definite orbits, much as planets revolve about the sun, are particles of matter called *electrons*. The electron is very light, being only about 1/1837 as heavy as a hydrogen atom; each electron carries 1 negative charge. A proton has a mass equal approximately to that of 1 hydrogen atom and carries 1 positive charge. The neutron is a neutral (uncharged) particle and has a mass a trifle greater than that of a proton. For all practical purposes the masses of protons and neutrons may be considered to be identical and equal to that of 1 hydrogen atom.

The number of protons is equal to the atomic number of the element.

Since the free element is neutral it must contain the same number of protons and electrons. Therefore the number of electrons in the free element is also equal to the atomic number.

Since the electrons have negligible weight, the mass of the atom is concentrated in the nucleus. That means that the sum of the neutrons and protons equals the mass number (approximately the atomic weight). Since the atomic number represents the number of protons, the difference between the mass number and the atomic number represents the number of neutrons.

The isotopes of an element have the same atomic number; that means that they must have the same number of electrons and also the same number of protons. Therefore isotopes of an element differ only in the number of neutrons in the nucleus. The term *nuclide* refers to any isotope of any element, that is, to any nucleus of definite mass.

One would expect, at first thought, that the mass of an atom would be the exact sum of the masses of its component neutrons, protons, and electrons. Actually, this is not true; the mass of the atom is slightly less. To illustrate, the mass of the helium atom is 0.0264 mass unit less than the sum of the masses of the 4 hydrogen atoms from which it can be considered to be derived. In the formation of a helium atom from 4 hydrogen atoms, 0.0264 mass unit of matter has disappeared; it has been converted directly into energy in accordance with the Einstein equation $E = mc^2$, in which E is the energy liberated, m is the mass of the matter lost, and c is the speed of light.

7.3 The arrangement of the electrons in the atom. All electrons lie outside the nucleus, and by comparison with the diameter of the nuclear mass, at relatively large distances from it. The atom, like our solar system, is mostly "space."

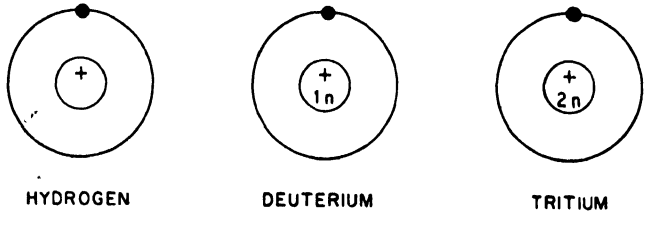


Figure 7.1. Pictorial representation of the structures of the atoms of hydrogen and its isotopes deuterium and tritium. ● represents an electron, + represents a proton and n represents a neutron. The center circle is the nucleus of the atom and the outer circle represents the shell in which the electron moves. Isotopes of an element have the same number of electrons and protons; they differ in the number of neutrons.

In line with the periodicity represented by the periodic table, the electrons are presumed to be located in *shells*, corresponding to the periods in the table. Within each shell they lie in *subshells*, corresponding to the various sequences of 2, 6, 10, and 14 electrons. Within each subshell the electrons are located in *orbitals*, with a maximum of 2 electrons falling in each orbital.

The hydrogen atom has an atomic number of 1; hence it has 1 electron moving about the nucleus in a definite orbit. The nucleus of the hydrogen isotope with a mass of 1 consists of 1 lone proton. The hydrogen isotope whose mass is 2 (deuterium) also has 1 electron, but its nucleus consists of 1 proton and 1 neutron. The hydrogen isotope with a mass of 3 (tritium) has 1 electron and a nucleus consisting of 1 proton and 2 neutrons. The scientists' concept of the atoms of the three hydrogen isotopes with all parts of the atom placed in one plane would be as represented by Figure 7.1.

Since helium has an atomic weight of 4 and an atomic number of 2, its atom will consist of 2 electrons, 2 protons, and 2 neutrons arranged as represented in Figure 7.2.

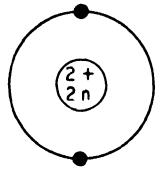


Figure 7.2. The helium atom.

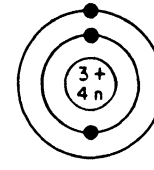


Figure 7.3. The lithium atom.

Helium is inert and it is the highest atomic-numbered element in the first period. Inertness of an element is interpreted to mean that its outer shell contains as many electrons as it can possibly hold; it is filled to its maximum capacity. That means that *the maximum number of electrons that can go into the first shell is 2.* The next element, lithium, whose atomic number is 3, can accordingly have no more than 2 electrons in its first shell; since it contains 3 electrons, the third is located in a second shell at a greater distance from the nucleus. The lithium atom will then appear as represented in Figure 7.3.

The atoms of Be, B, C, O, F, and Ne will then have the structures represented in Figure 7.4. Note that each new structure is created by adding 1 electron and 1 proton to the structure of the preceding element. The relationship between the number of neutrons in the atoms of two consecutive elements will depend upon which particular isotope of each element is being used for comparison. Thus C^{12} has 1 more neutron than

B^{10}, but the same number as B^{11}, and K^{39} has 2 neutrons fewer than A^{40}. As already noted, the sum of the protons and neutrons equals the mass number of the nuclide.

Neon is an inert gas. It has 8 electrons in its outer shell. Using the neon atom as the basis for our conclusion, we will postulate that when an outer shell acquires 8 electrons the resulting element is an inert gas. That means that each of the inert gases in group 0 has 8 electrons in its outer shell. Once an inert gas structure of 8 outer-shell electrons is reached, the next electron that is added must fall in the next shell.

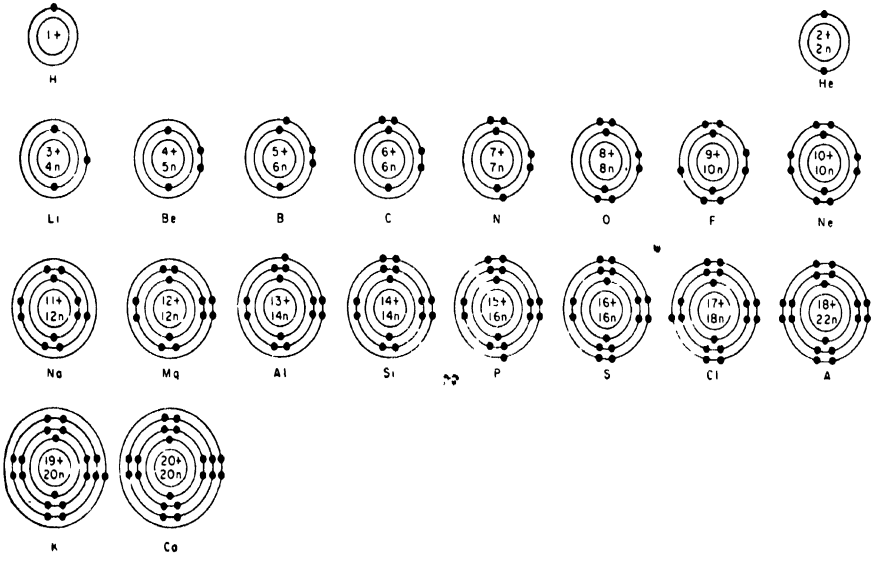


Figure 7.4. The atomic structures of the first 20 elements. These diagrams indicate, schematically, the number of electrons that fall in each shell and the number of protons and electrons in a nuclide of each element. They are not intended to represent the actual or relative sizes of the atoms. The actual diameters of the atoms are given in Figure 7.7.

That means that this next atom will have 1 electron in its outer shell. That, we note in Figure 7.4, is true in the case of Na, which follows Ne. The outer shell of the Na atom is, we observe, the same as the outer shell of the Li atom. We have already noted in Section 6.1 that Li and Na are chemically similar; in line with this similarity they both fall in group IA of the periodic table. What we are doing now is to account for the similarity by giving them the same outer-shell electron configuration. Because the outer-shell electrons of an element are responsible for its chemical properties and its combining capacity, they are commonly referred to as *valence electrons*.

We note in Figure 7.4 that, as in the case of Li and Na, the Be and Mg, B and Al, C and Si, N and P, O and S, F and Cl, and Ne and A outer shells are also identical. As in the case of Li and Na, the experimental evidence cited in Section 6.1 shows that the two elements in each pair are chemically similar. To account for this similarity, the modern concept of the atom gives each of the two similar elements identical outer-shell electron configurations. Having accounted for the chemical similarity of elements by giving them identical outer-shell electron configurations, we can then state, as a guide to the study of the elements, that *when elements have identical outer-shell electron structures they are chemically similar.* If the structures of all the elements of the table were before us we would find that *in each of the A groups, and in group* 0, *the outer shells of all elements in the group are identical.* Stated differently, *in each of the A groups and group* 0 *all the elements in the group have the same number of valence electrons; this number corresponds, in each of the A groups, to the number of the group.*

The new electron that is added in going from the inert gas argon to potassium must go into a new outer shell. This means that potassium has 1 electron in its outer shell (see Figure 7.4). That should make it chemically similar to Na; we have learned in Section 6.1 that K is similar to Na. There is 1 more electron in the calcium structure than in the potassium structure. This gives the calcium atom 2 valence electrons and throws it into the group and class with Be and Mg, where the experimental evidence shows that it belongs.

We see from what has been stated that by using the periodic table as a guide, representation of the electron structures of the first 20 elements is a simple matter of adding electrons, in an orderly fashion, up to a total of 2 in the first shell and 8 in each of the next two shells.

When we go beyond calcium, the structures are complicated by the introduction of the 10-element sequences of transition metals in periods 4 and 5, and the 14-member lathanide series and the 10-element sequence of transition elements in period 6. To understand the description of these structures we must say something about the *subshells* and *orbitals* into which electrons fall.

The first 2 electrons that enter any shell are referred to as the s electrons. The next 6 electrons that enter any shell are the p electrons, and the level at which they enter is called the p subshell; the orbitals in this subshell are p orbitals. The next 10 electrons that enter a shell are d electrons and enter the d subshell; the orbitals in this subshell are d orbitals. The last 14 electrons that enter a shell are f electrons; they enter the f subshell, and they occupy f orbitals.

The maximum number of each type of electron that can enter any one shell is: $s = 2$, $p = 6$, $d = 10$, and $f = 14$; p electrons do not enter a shell until the maximum of 2 s electrons have already entered; d electrons do not enter a shell until the maximum number of p's have entered, and f's do not enter until the

maximum number of *d*'s have entered. The reason for the latter concept is that, in any shell, the energy required to bring in an *s* electron is less than that for a *p* electron, which is less than that for a *d* electron, which is less than that for an *f* electron. The process that requires the least energy will take place first.

Since H and He have 1 and 2 electrons, respectively, these must be *s* electrons. The electron structure of an atom is derived by adding 1 electron to the structure of the preceding atom. (This does not mean that an element can be *prepared* by adding 1 electron to the preceding element.) Thus the structures of the elements in group IA are, in every instance, derived from an inert gas structure by adding 1 electron to the next shell. (At the moment we are not concerned about the 1 proton and variable numbers of neutrons involved in going from the complete structure of one atom to the complete structure of the next one.) It follows that the 1 outer-shell electron in the Li atom must be an *s* electron. The same will apply to the lone valence electron in Na, K, Rb, Cs, and Fr. That means that each group IA element contains 1 *s* electron in the valence shell. Likewise each of the group IIA elements, Be, Mg, Ca, Sr, Ba, and Ra contains 2 *s* valence electrons. Stated differently, the valence electrons that produce the IA and IIA elements are *s* electrons. This is indicated in the periodic table by calling the group IA and IIA elements the *s* electron elements.

There is 1 more electron in the boron structure than in the beryllium structure. This 1 electron goes into the same shell as the 2 *s* electrons in the beryllium structure. Therefore, by definition, it must be a *p* electron and it must fall in a *p* orbital. That means that the outer shell of the boron atom contains 2 *s* electrons and 1 *p* electron. The inner shell (first shell) contains 2 *s* electrons. We can designate the structure of the boron atom by the notation $1s^2$, $2s^2$, $2p^1$. The number 1 in front of the *s* in the notation $1s^2$ means the number of the shell, the *s* refers to the kind of electron, and the superscript 2 refers to the number of these electrons. The notation $2p^1$ means "one *p* electron in the second shell." The 1 electron that is added to the boron structure to give the carbon structure is a *p* electron. Likewise, the 1 electron that is added to the structures of C, N, O, and F to yield, respectively, the structures of N, O, F, and Ne is in each case a *p* electron. Remember, the first 2 electrons that enter a shell are *s* electrons, and the next 6 are *p* electrons. The shorthand designation of the structure of the neon atom will be $1s^2$, $2s^2$, $2p^6$. (See Table 7.3 for the detailed electronic configurations of all atoms.)

If we analyze all the group IIIA, IVA, VA, VIA, VIIA, and 0 elements as we have done B, C, N, O, F, and Ne, we will find that in every case the electron which produces each structure when added to the structure of the atom of next lower atomic number is a *p* electron. For that reason the elements in groups IIIA, IVA, VA, VIA, VIIA, and 0 are designated in the periodic table as the *p electron elements.*

To build up the structures of the B group elements in periods 4 and 5, we must call upon *d* electrons. Because the last element in each period is an inert gas and because as already stated, the element which follows an inert gas must have 1 electron in the next shell, K, Rb, Cs, and Fr in group IA each have

one s electron in the outer shell. The elements Ca, Sr, Ba, and Ra in group IIA will then each have 2 s electrons. The five elements which precede the inert gas at the end of each period will have, respectively 3, 4, 5, 6, and 7 valence electrons, and all but the first 2 of them will be p electrons. That means that Ga in group IIIA of period 4 will have 3 outer-shell (valence) electrons. Since Ca has 2 outer shell electrons one can conclude that the 10 electrons that are added, successively, in period 4, creating the structures of Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, from the Ca structure, must either have been slipped directly into the next lower shell, shell 3, or they must have replaced 4s electrons which have slipped into shell 3. Since shell 3 already has its full quota of 2 s and 6 p electrons, these new electrons that it receives in order to yield the Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn structures must by definition be d electrons. Since they fall in the third shell they are referred to as 3d electrons. Since these 3d electrons fall into the third shell after the two 4s electrons are added to the fourth shell but before the six 4p electrons that yield the Ga, Ge, As, Se, Br, and Kr structures are added to the fourth shell, they must be at a higher energy level than the 4s electrons but a lower energy level than the 4p electrons.

If the 10 electrons that are added to the calcium structure to give the Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn structures simply fell directly into the 3d orbitals one after another, setting up the structures would be simple because the arrangement of these 3d electrons and the two 4s electrons present in the original calcium structure would be as represented in the 2 left columns of Table 7.1.

TABLE 7.1

STRUCTURES OF FOURTH PERIOD, B GROUP ATOMS

Ideal Arrangement				*Actual Arrangement*	
No. of 3d electrons	*No. of 4s electrons*	*Atomic number*	*Element*	*No. of 3d electrons*	*No. of 4s electrons*
0	2	20	Ca	0	2
1	2	21	Sc	1	2
2	2	22	Ti	2	2
3	2	23	V	3	2
4	2	24	Cr	5	1
5	2	25	Mn	5	2
6	2	26	Fe	6	2
7	2	27	Co	7	2
8	2	28	Ni	8	2
9	2	29	Cu	10	1
10	2	30	Zn	10	2

The actual structures, as revealed by physical measurements which are too complex to consider in a book of this scope, are as represented in the two right-hand columns of Table 7.1. The data in this table indicate that formation of an atom by addition of a d electron (plus 1 proton and a variable number of neutrons) to a lower structure may be accompanied by a shift in the position of electrons from one subshell to another. This fact is, we shall find, of great

significance in accounting for the properties of the B group elements. It means also that one cannot develop the electronic structures of the atoms of these elements in a simple, orderly manner as is the case with the A and O group elements.

The structures of the elements beyond Zn in period 4 are formed by adding $4p$ electrons to the Zn structure. The structure of bromine will then be

$$1s^2,\ 2s^2,\ 2p^6,\ 3s^2,\ 3p^6,\ 4s^2,\ 3d^{10},\ 4p^5,\ \text{or}$$
$$1s^2,\ 2s^2,\ 2p^6,\ 3s^2,\ 3p^6,\ 3d^{10},\ 4s^2,\ 4p^5$$

The structures of the elements in period 5 are built up from the strontium structure in the same way that the period 4 elements are built up from the calcium structure. The number of $5s$ and $4d$ electrons in the strontium and B group element structures of period 5 are given in Table 7.2.

TABLE 7.2

STRUCTURE OF THE FIFTH PERIOD B GROUP ATOMS

At. no.	*Element*	*No. of 4d electrons*	*No. of 5s electrons*
38	Sr	0	2
39	Y	1	2
40	Zr	2	2
41	Nb	4	1
42	Mo	5	1
43	Tc	6	1
44	Ru	7	1
45	Rh	8	1
46	Pd	10	0
47	Ag	10	1
48	Cd	10	2

The structure of the tin atom, which is formed by the addition of two $5p$ electrons to the cadmium structure, is given in Figure 7.5. To show the addition feature of the structure of an atom, the tin atom is resolved into some of its predecessors. The cadmium structure is formed by adding ten $4d$ electrons to the strontium structure, the strontium structure is formed by adding two $5s$ electrons to the krypton structure, and so on. Here again it should be emphasized that cadmium cannot be *prepared* by adding ten $4d$ electrons to strontium.

The detailed electronic configurations of the elements in periods 4 and 5 are shown in Table 7.3.

In period 6 the lanthanum structure (57) is formed by the addition of one $5d$ electron to the barium structure. In the formation of the structures of the next 14 elements, the lanthanides, Ce (58) to Lu (71), electrons are added directly or indirectly in the fourth shell. Since the fourth shell already contains its full quota of 2 s electrons, 6 p electrons, and 10 d electrons, these new electrons must be f electrons. Since they are f electrons they cannot be added to the fifth shell because it does not yet have its full quota of 10 d electrons. The detailed electron configuration of the 14 lanthanides is shown in Table 7.3. Because they are

formed by addition of f electrons they are referred to in the periodic table as *f electron elements*. The remaining B group elements structures in period 6, namely, Hf, Ta, W, Re, Os, Ir, Pt, Au, and Hg, are formed by addition of 5 d electrons to the lutecium (71) structure. These configurations are shown in Table 7.3. The remaining A group element structures in period 6 are formed by addition of 6 p electrons to the mercury structure. Their configurations are shown in Table 7.3.

It will be noted in Table 7.3 that just as the lanthanum structure (57) is formed by addition of one 5 d electron to the barium structure (56), so the actinium structure (89) which falls in the same group (IIIB) as lanthanum, is formed by addition of one 6 d electron to the radium structure (88). All the actinides except thorium are formed by addition of 5 f electrons to the actinium structure.

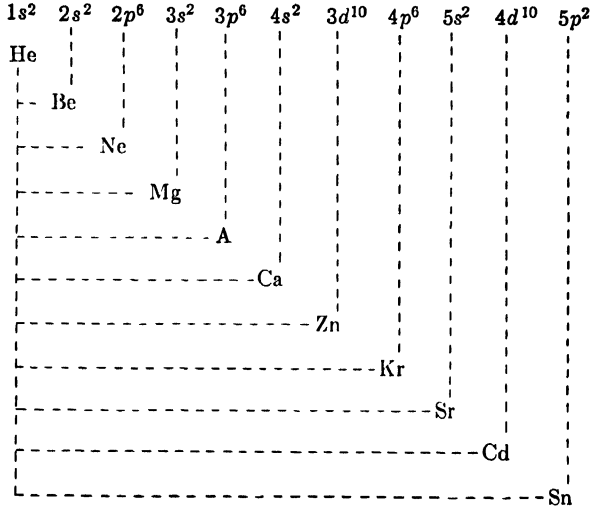


Figure 7.5. Resolution of the tin atom.

Figure 7.6 shows how the electronic configuration of an atom is related to its position in the periodic table. It points out the orderly fashion in which atoms are built up.

The correlation between the position of the element in the periodic table and the subshell in which electrons are added may be summarized as follows.

1. Group IA and IIA elements have, respectively, 1 and 2 s electrons of the shell in which they fall in their valence shells.

2. Group IIIA, IVA, VA, VIA, VIIA, and 0 elements have 2 s electrons and 3 to 6, respectively, p electrons of the shell in which they fall in their valence shells.

3. The B groups in periods 4 and 5 are built up with d electrons in a lower shell.

TABLE 7.3

ELECTRONIC CONFIGURATION OF THE ATOMS OF THE ELEMENTS

Number of electrons in each subshell

At. no.	*Symbol*	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	7*s*
								Period 1											
1	H	1																	
2	He	2																	
								Period 2											
3	Li	2	1																
4	Be	2	2																
5	B	2	2	1															
6	C	2	2	2															
7	N	2	2	3															
8	O	2	2	4															
9	F	2	2	5															
10	Ne	2	2	6															
								Period 3											
11	Na	2	2	6	1														
12	Mg	2	2	6	2														
13	Al	2	2	6	2	1													
14	Si	2	2	6	2	2													
15	P	2	2	6	2	3													
16	S	2	2	6	2	4													
17	Cl	2	2	6	2	5													
18	A	2	2	6	2	6													
								Period 4											
19	K	2	2	6	2	6		1											
20	Ca	2	2	6	2	6		2											
21	Sc	2	2	6	2	6	1	2											
22	Ti	2	2	6	2	6	2	2											
23	V	2	2	6	2	6	3	2											

ELECTRONIC CONFIGURATION OF THE ATOMS OF THE ELEMENTS

		Number of electrons in each subshell																	
At. no.	*Symbol*	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	7*s*
24	Cr	2	2	6	2	6	5	1											
25	Mn	2	2	6	2	6	5	2											
26	Fe	2	2	6	2	6	6	2											
27	Co	2	2	6	2	6	7	2											
28	Ni	2	2	6	2	6	8	2											
29	Cu	2	2	6	2	6	10	1											
30	Zn	2	2	6	2	6	10	2											
31	Ga	2	2	6	2	6	10	2	1										
32	Ge	2	2	6	2	6	10	2	2										
33	As	2	2	6	2	6	10	2	3										
34	Se	2	2	6	2	6	10	2	4										
35	Br	2	2	6	2	6	10	2	5										
36	Kr	2	2	6	2	6	10	2	6										
		Period 5																	
37	Rb	2	2	6	2	6	10	2	6			1							
38	Sr	2	2	6	2	6	10	2	6			2							
39	Y	2	2	6	2	6	10	2	6	1		2							
40	Zr	2	2	6	2	6	10	2	6	2		2							
41	Nb	2	2	6	2	6	10	2	6	4		1							
42	Mo	2	2	6	2	6	10	2	6	5		1							
43	Tc	2	2	6	2	6	10	2	6	6		1							
44	Ru	2	2	6	2	6	10	2	6	7		1							
45	Rh	2	2	6	2	6	10	2	6	8		1							
46	Pd	2	2	6	2	6	10	2	6	10									
47	Ag	2	2	6	2	6	10	2	6	10		1							
48	Cd	2	2	6	2	6	10	2	6	10		2							
49	In	2	2	6	2	6	10	2	6	10		2	1						

TABLE 7.3 (*Cont.*)

ELECTRONIC CONFIGURATION OF THE ATOMS OF THE ELEMENTS

Number of electrons in each subshell

At. no.	*Symbol*	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	7*s*
50	Sn	2	2	6	2	6	10	2	6	10		2	2						
51	Sb	2	2	6	2	6	10	2	6	10		2	3						
52	Te	2	2	6	2	6	10	2	6	10		2	4						
53	I	2	2	6	2	6	10	2	6	10		2	5						
54	Xe	2	2	6	2	6	10	2	6	10		2	6						
								Period 6											
55	Cs	2	2	6	2	6	10	2	6	10		2	6			1			
56	Ba	2	2	6	2	6	10	2	6	10		2	6			2			
57	La	2	2	6	2	6	10	2	6	10		2	6	1		2			
58	Ce	2	2	6	2	6	10	2	6	10	2	2	6			2			
59	Pr	2	2	6	2	6	10	2	6	10	3	2	6			2			
60	Nd	2	2	6	2	6	10	2	6	10	4	2	6			2			
61	Pm	2	2	6	2	6	10	2	6	10	5	2	6			2			
62	Sm	2	2	6	2	6	10	2	6	10	6	2	6			2			
63	Eu	2	2	6	2	6	10	2	6	10	7	2	6			2			
64	Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
65	Tb	2	2	6	2	6	10	2	6	10	9	2	6			2			
66	Dy	2	2	6	2	6	10	2	6	10	10	2	6			2			
67	Ho	2	2	6	2	6	10	2	6	10	11	2	6			2			
68	Er	2	2	6	2	6	10	2	6	10	12	2	6			2			
69	Tm	2	2	6	2	6	10	2	6	10	13	2	6			2			
70	Yb	2	2	6	2	6	10	2	6	10	14	2	6			2			
71	Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
72	Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
73	Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
74	W	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
75	Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2			

TABLE 7.3 (*Cont.*)

ELECTRONIC CONFIGURATION OF THE ATOMS OF THE ELEMENTS

Number of electrons in each subshell

At. no.	*Symbol*	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*	4*s*	4*p*	4*d*	4*f*	5*s*	5*p*	5*d*	5*f*	6*s*	6*p*	6*d*	7*s*
76	Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
77	Ir	2	2	6	2	6	10	2	6	10	14	2	6	9					
78	Pt	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
79	Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
80	Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
81	Tl	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
82	Pb	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
83	Bi	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
84	Po	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
85	At	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
86	Rn	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
									Period 7										
87	Fr	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
88	Ra	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
89	Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	1
90	Th	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
91	Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
92	U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
93	Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
94	Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	5	2	6	1	2
95	Am	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	1	2
96	Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
97	Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
98	Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	9	2	6	1	2
99		2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	1	2
100		2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	1	2

Figure 7.6

Electron Configuration of the Elements and Their Positions in the Periodic Table

Period	Orbitals	s		d									p (except He)					
	Character	Light metals		Heavy metals									Nonmetals					Inert gases
	Group	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1	*	1 H 1																2 He 2
2	*	3 Li 1	4 Be 2										5 B 3	6 C 4	7 N 5	8 O 6	9 F 7	10 Ne 8
3	*	11 Na 1	12 Mg 2										13 A 3	14 S 4	15 P 5	16 S 6	17 Cl 7	18 A 8
4	*	19 K 8, 1	20 Ca 8, 2	21 Sc 9, 2	22 Ti 10, 2	23 V 11, 2	24 Cr 13, 1	25 Mn 13, 2	26 Fe 14, 2	27 Co 15, 2	28 Ni 16, 2	29 Cu 18, 1	30 Zn 18, 2	31 Ga 18, 3	32 Ge 18, 4	33 As 18, 5	34 Se 18, 6	35 Br 18, 7	36 Kr 18, 8
5	*	37 Rb 8, 1	38 Sr 8, 2	39 Y 9, 2	40 Zr 10, 2	41 Nb 12, 1	42 Mo 13, 1	43 Tc 14, 1	44 Ru 15, 1	45 Rh 16, 1	46 Pd 18, 0	47 Ag 18, 1	48 Cd 18, 2	49 In 18, 3	50 Sn 18, 4	51 Sb 18, 5	52 Te 18, 6	53 I 18, 7	54 Xe 18, 8
6	*	55 Cs 18, 8, 1	56 Ba 18, 8, 2	57 La 18, 9, 2	72 Hf 32, 10, 2	73 Ta 32, 11, 2	74 W 32, 12, 2	75 Re 32, 13, 2	76 Os 32, 14, 2	77 Ir 32, 17, 0	78 Pt 32, 17, 1	79 Au 32, 18, 1	80 Hg 32, 18, 2	81 Tl 32, 18, 3	82 Pb 32, 18, 4	83 Bi 32, 18, 5	84 Po 32, 18, 6	85 At 32, 18, 7	86 Rn 32, 18, 8
7	*	87 Fr 18, 8, 1	88 Ra 18, 8, 2	89 Ac 18, 9, 2															

Transition elements

* Atomic number
Symbol
Electron configuration. (Number of electrons in each shell. Base structure given in square marked *)

	f orbitals													
Lanthanides Group IIIB 2, 8, 18	58 Ce 20, 8, 2	59 Pr 21, 8, 2	60 Nd 22, 8, 2	61 Pm 23, 8, 2	62 Sm 24, 8, 2	63 Eu 25, 8, 2	64 Gd 25, 9, 2	65 Tb 27, 8, 2	66 Dy 28, 8, 2	67 Ho 29, 8, 2	68 Er 30, 8, 2	69 Tm 31, 8, 2	70 Yb 32, 8, 2	71 Lu 32, 9, 2
Actinides 2, 8, 18, 32	90 Th 18, 10, 2	91 Pa 20, 9, 2	92 U 21, 9, 2	93 Np 22, 9, 2	94 Pu 23, 9, 2	95 Am 24, 9, 2	96 Cm 25, 9, 2	97 Bk 26, 9, 2	98 Cf 27 9, 2	99	100			

4. The B groups in periods 6 and 7 are built up with *d* and *f* electrons in the lower shells.

7.4 The diameters of the atoms. The diameters of the atoms of the elements have been *calculated* from certain types of data whose discussion is beyond a book of this scope. These calculations assume that the atom is spherical. The values are given in Figure 7.7. An examination of the data in Figure 7.7 reveals certain interesting relationships between the diameter of an atom and its position in the periodic table.

1. *In any periodic group, as the atomic number of the element increases, its atomic diameter increases.* This is consistent with the concept that the electrons are arranged in shells built up one outside the other. As the number of shells increases, the diameter of the atom would be expected to increase. Exceptions to this increase in diameter with increase in atomic number are noted in groups IVB, IB, and IIB. We will learn as our study progresses that the B group elements show numerous irregularities.

2. *In any periodic period, as the atomic number increases the atomic diameter decreases.* This is exactly true in periods 2 and 3 and is approximately true in periods 4, 5, and 6. Here again, the irregularities appear in the B groups. If the B groups are ignored the rule applies to all periods. The fact that the diameter decreases with increasing atomic number in a period is consistent with the idea that all valence electrons in any period lie in one shell. As the number of valence electrons increases and the positive charge on the nucleus increases, there will be a tendency for the shells to be drawn in and the diameter of the atom to be decreased.

7.5 The density of a solid element and the diameter of its atom. Since a crystal is formed when the atoms of an element arrange themselves in a definite pattern, it will be of interest to note how the density of the crystal of a solid element varies with the mass (gram-atomic weight) and diameter of its component atoms. Figure 7.8 gives this information. An examination of Figure 7.8 brings out the following relationships.

1. *In any group, as the atomic weight increases, the density of the solid element increases.* Minor exceptions to this rule are noted only in the case of the lighter members of groups IA and IIA.

2. *In any period the density increases to a maximum as the atomic weight increases, and then decreases.* This decrease in density after the maximum has been passed takes place even though the atomic weight is increasing and the atomic diameter is decreasing. It is of interest to note that the B group elements have relatively high densities and that the group VIIIB metals have the maximum densities in periods 4, 5, and 6.

Figure 7.7

The Atomic Diameters of the Elements in Relation to Their Positions in the Periodic Table

Period	Character	Light metals		Heavy metals										Non-metals					
	Orbitals	*s*		*d*										*p* (except He)					
	Group	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1	*	1 H																	2 He
2	*	3 Li 2.45	4 Be 1.78											5 B 1.60	6 C 1.54	7 N 1.48	8 O 1.48	9 F 1.44	10 Ne
3	*	11 Na 3.14	12 Mg 2.73											13 Al 2.50	14 Si 2.35	15 P 2.20	16 S 2.08	17 Cl 1.99	18 A
				Transition elements															
4	*	19 K 4.05	20 Ca 3.47	21 Sc 2.88	22 Ti 2.65	23 V 2.45	24 Cr 2.34	25 Mn 2.34	26 Fe 2.33	27 Co 2.31	28 Ni 2.30	29 Cu 2.35	30 Zn 2.50	31 Ga 2.49	32 Ge 2.45	33 As 2.42	34 Si 2.34	35 Br 2.28	36 Kr
5	*	37 Rb 4.32	38 Sr 3.83	39 Y 3.23	40 Zr 2.91	41 Nb 2.68	42 Mo 2.58	43 Tc	44 Ru 2.48	45 Rh 2.49	46 Pd 2.56	47 Ag 2.68	48 Cd 2.83	49 In 3.00	50 Sn 2.82	51 Sb 2.82	52 Te 2.74	53 I 2.67	54 Xe
6	*	55 Cs 4.70	56 Ba 3.96	57 La 3.38	72 Hf 2.88	73 Ta 2.69	74 W 2.60	75 Re 2.56	76 Os 2.51	77 Ir 2.52	78 Pt 2.58	79 Au 2.67	80 Hg 2.88	81 Tl 3.10	82 Pb 3.08	83 Bi 3.04	84 Po 3.06	85 At	86 Rn
7	*	87 Fr	88 Ra	89 Ac															

* Atomic number
Symbol
Atomic diameter Å

	f orbitals													
Lanthanides Group IIIB	58 Ce 3.29	59 Pr 3.30	60 Nd 3.28	61 Pm	62 Sm 3.32	63 Eu 3.70	64 Gd 3.23	65 Tb 3.18	66 Dy 3.18	67 Ho 3.16	68 Er 3.13	69 Tm 3.12	70 Yb 3.40	71 Lu 3.11
Actinides	90 Th 3.30	91 Pa	92 U 2.84	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99	100			

FIGURE 7.8

RELATION BETWEEN THE DENSITY OF A SOLID AND ITS ATOMIC DIAMETER, ATOMIC WEIGHT AND POSITION IN THE PERIODIC TABLE

Period	Orbitals	*s*		*d*										*p* (except He)					Inert gases
	Character	Light metals		Heavy metals										Nonmetals					
	Group	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1	*	1.008 H																	4.003 He
2	*	6.940 Li 2.45 0.53	9.013 Be 1.78 1.86											10.82 B 1.60 2.45	12.01 C 1.54 2.25	14.01 N 1.48 —	16.00 O 1.48 —	19.00 F 1.44 —	20.18 Ne
3	*	23.00 Na 3.14 0.97	24.32 Mg 2.73 1.75											26.97 Al 2.50 2.70	28.06 Si 2.35 2.40	30.98 P 2.20 1.82	32.07 S 2.08 2.07	35.46 Cl 1.99 —	39.94 A
4	*	39.10 K 4.05 0.86	40.08 Ca 3.47 1.55	45.10 Sc 2.88 3.0	47.90 Ti 2.65 4.5	50.95 V 2.45 6.0	52.01 Cr 2.34 7.1	54.93 Mn 2.34 7.2	55.85 Fe 2.33 7.86	58.94 Co 2.31 8.90	58.69 Ni 2.30 8.90	63.54 Cu 2.35 8.92	65.38 Zn 2.50 7.14	69.72 Ga 2.49 5.90	72.60 Ge 2.45 5.36	74.91 As 2.42 5.73	78.96 Se 2.34 4.79	79.92 Br 2.28 —	83.7 Kr
5	*	85.48 Rb 4.32 1.53	87.63 Sr 3.83 2.60	88.92 Y 3.23 5.5	91.22 Zr 2.91 6.5	92.91 Nb 2.68 8.4	95.95 Mo 2.58 10 2	99 Tc — —	101.7 Ru 2.48 12.2	102.9 Rh 2.49 12.5	106.7 Pd 2.56 12.2	107.9 Ag 2.68 10.5	112.4 Cd 2.83 8.64	114.8 In 3.00 7.3	118.7 Sn 2.82 7.31	121.8 Sb 2.82 6.68	127.6 Te 2.74 6.25	126.9 I 2.67 4.93	131.3 Xe
6	*	132.9 Cs 4.70 1.90	137.4 Ba 3.96 3.61	138.9 La 3.38 6.2	178.6 Hf 2.88 13.3	180.9 Ta 2.69 16.6	183.9 W 2.60 19.3	186.3 Re 2.56 20.5	190.2 Os 2.51 22.5	193.1 Ir 2.52 22.4	195.2 Pt 2.58 21.4	197.2 Au 2.67 19.3	200.6 Hg 2.88 —	204.4 Tl 3.10 11.9	207.2 Pb 3.08 11.3	209.0 Bi 3.04 9.80	210 Po 3.06 —	211 At	222 Rn
7	*	223 Fr	226.1 Ra — 5.0	227 Ac															

* Atomic weight
Symbol
Atomic diameter Å
Density of solid element g/cc

Transition elements

7.6 Transfer of electrons. Electrovalence. Having gotten a picture of what is believed to be the structure of the atom the question now arises, Just what happens when atoms of different elements combine to form compounds? *Atoms of one element combine with atoms of another element to form a compound either by transfer of electrons or by sharing pairs of electrons.* Thus, in the combination of 1 atom of sodium, which has 1 electron in its outer shell, with 1 atom of chlorine, which has 7 electrons in its outer shell, to form the compound, NaCl, the 1 sodium valence electron is transferred from the sodium atom to the outer shell of the chlorine atom. Just why does sodium give up its electron and why does chlorine accept it? The theory dealing with the behavior of elements postulates that every atom tries to achieve the stable structure of the nearest inert gas, that is, it tries to acquire an 8-electron shell (or a 2-electron shell if the nearest inert gas is helium). (This rule applies, strictly, only to the A group elements.) If giving away electrons to form the lower inert gas structure is the easiest way to reach an inert gas structure, that is what the atom will do. If receiving additional electrons to form the higher inert gas is the easiest way to attain the objective, the atom will take up electrons. Atoms with 1, 2, and 3 valence electrons find it easier to give away electrons, those with 4, 5, 6, and 7 find it easier to receive them. In the case of the sodium and chlorine atoms, sodium gives one electron and chlorine receives one.

To start with, the sodium atom was neutral, with 11 protons and 12 neutrons in its nucleus and 11 electrons outside the nucleus. After it has given away its 1 valence electron it has 11 protons and 10 electrons, or an excess of 1 proton. It no longer is a neutral atom; it has become an *ion* with a positive charge. Likewise, the chlorine atom which originally was neutral because of its 17 protons and 17 electrons has become an ion with 1 negative charge because it contains 17 protons and 18 electrons. The evidence to support the belief that electrons are transferred and ions are formed is the fact that melted NaCl is a conductor of electricity; during the conductivity process sodium metal collects at the negative pole of the cell and chlorine collects at the positive pole. This indicates that the sodium ion is positively charged, while the chlorine ion is negatively charged. Because it has given up 1 electron to form an ion with 1 positive charge, sodium is said to have an oxidation number of +1 in this ion and the ion is said to have an *electrovalence* of +1. Since sodium gives up an electron to form a positive ion, it is said to be *electropositive*, and since its tendency to give up this electron is very strong, as indicated by the vigor with which it reacts, it is said to be *strongly electropositive*. Because the chlorine atom readily accepts an electron and thereby becomes a negative ion, it is

said to be strongly *electronegative*. The chloride ion has an electrovalence of -1, and chlorine, in this chloride ion, has an oxidation number of -1. The process that takes place when NaCl is formed by combination of sodium and chlorine is represented in Figure 7.9.

An atom of magnesium, which has 2 valence electrons, will, when it reacts with chlorine, transfer these 2 electrons to 2 atoms of chlorine. As a result there will be formed 1 magnesium ion with an electrovalence

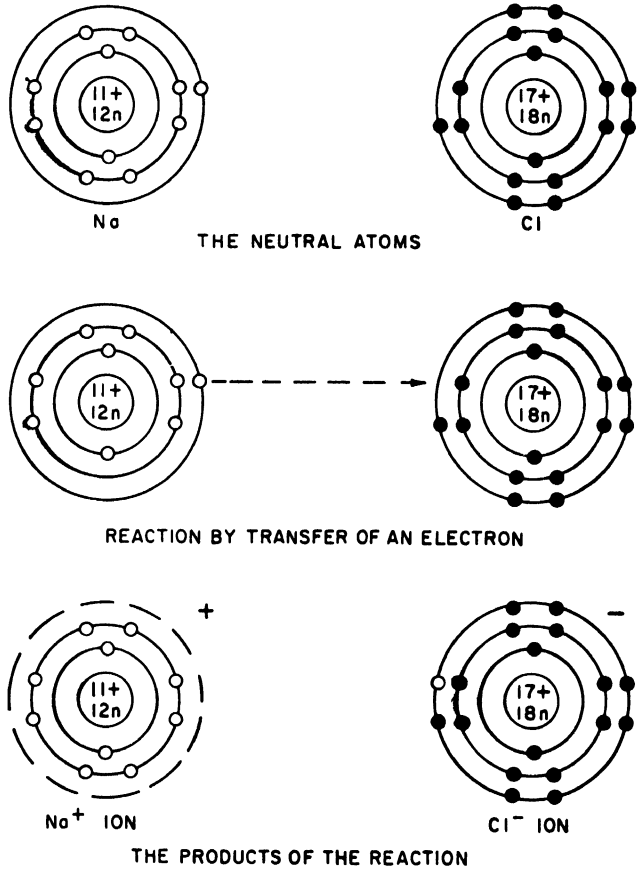


Figure 7.9. Combination of sodium with chlorine to form the electrovalent compound sodium chloride. This compound is made up of positive sodium ions and negative chloride ions. The sodium atom has given up its one valence electron and has thereby acquired the stable inert-gas electron configuration of the neon atom. The chlorine atom has received one valence electron and has thereby acquired the stable inert-gas electron configuration of the argon atom. Note that the nucleus of each atom is unchanged.

of +2 (Mg^{++}), and 2 chloride ions, each with an electrovalence of −1. The oxidation number of the magnesium in its ion is +2; the electrovalence of the Mg^{++} ion is +2. The gallium atom, which has 3 valence electrons, will form the Ga^{+++} ion, in which its oxidation number is +3, by the transfer of these three electrons to 3 atoms of chlorine; this ion will have an electrovalence of +3.

An examination of the periodic table (Figure 7.6) and Table 7.3 shows that most metals have 1, 2, or 3 electrons in their valence shells; a few have 4. As a result, they tend to react as do sodium and magnesium, giving off their electrons and forming positive ions. *Metals as a class are therefore electropositive.* The ease with which they give off their electrons to form ions is referred to as their *electropositivity.* The more easily a metal gives off its electrons, the greater its tendency to react with another element. That means that its tendency to react is directly proportional to its electropositivity. The reactivity table of the metals (Table 3.3) can therefore correctly be called the *electropositivity table.*

Just as the metals give off electrons to form positive ions because they have 4 or fewer electrons in their valence shells, so nonmetals tend to receive electrons because they have 4 or more valence electrons. *Nonmetals as a class are therefore electronegative,* and the vigor with which they accept electrons is a measure of their electronegativity. The reactivity table of the nonmetals (Table 3.4) could just as well be labeled the *electronegativity table.*

It follows from what has been stated that binary compounds formed by the combination of a metal with a nonmetal will be electrovalent and ionic in character. Experimental evidence shows that ternary compounds, such as Na_2SO_4, in which a metal is combined with a nonmetal radical, also are ionic in character and must therefore have been formed by the transfer of electrons. Compounds in which a metal is combined with a nonmetal or nonmetal radical are called *salts* (see Chapter 4). One can conclude therefore that *all salts are electrovalent compounds and are ionic in character. Metal oxides and hydroxides also are ionic and electrovalent.* To designate their ionic character, the simple formulas of these electrovalent compounds (salts, metal oxides, metal hydroxides) are sometimes written in the form Na^+Cl^-, $Ca^{++}SO_4^{--}$, $Mg^{++}O^{--}$. Most authors, however, make no reference to the charges on the ions but use the simple unlabeled formulas such as KCl, $CuSO_4$, NaOH, etc.

7.7 Diameters of ions. The diameters of the positive and negative ions in the solid crystals of electrovalent binary compounds have been calculated from x-ray measurements. The results show that:

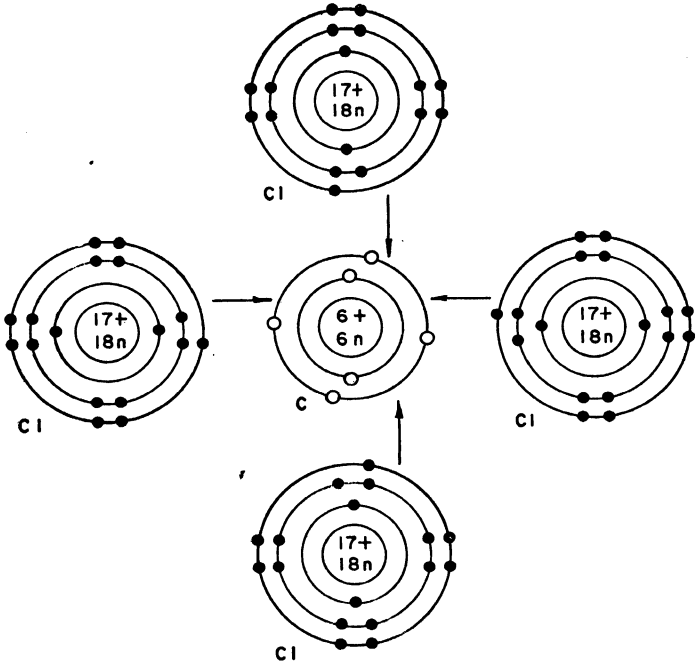
1. *A positive ion is always smaller than the parent atom.* This is in line with the concept that the electrons are arranged in shells, that the valence electrons lie in the outer shell, and that the formation of a positive ion consists in the loss of these valence electrons.

2. *A negative ion is always larger than the parent atom.* This is in line with the concept that negative ions are formed by the addition of electrons to the valence shell.

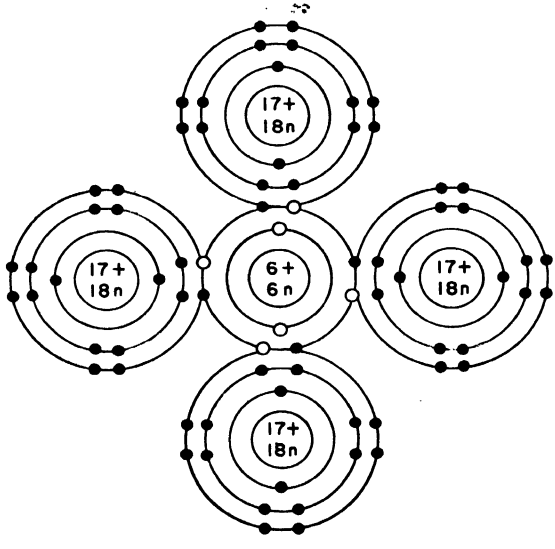
7.8 Sharing of electrons. Covalence. If all compounds were formed as a result of the transfer of electrons, they would all be ionic in character and would therefore all be electric conductors in the melted state. The experimental fact is that a great many compounds are not electric conductors in the melted state, are therefore not ionic in character, and must therefore not have been formed by transfer of electrons. Such compounds are believed to be formed by mutual *sharing of pairs of electrons.* As a result of this mutual sharing of pairs of electrons, the atoms of both elements attain an inert gas structure. To illustrate, liquid CCl_4 is a nonconductor. When the CCl_4 molecule is formed by the combination of 1 atom of carbon with 4 atoms of chlorine, the 5 atoms are so arranged in the molecule that each of the 4 carbon valence electrons fits into the outer shell of a chlorine atom, thereby giving it the inert-gas structure. In return, 1 electron from each of the 4 chlorine valence shells fits into the carbon valence shell. It is an even-exchange sort of a deal whereby each atom both gives and receives. Each chlorine atom ends up with 8 electrons in its valence shell; 7 of its own and 1 from the carbon atom. The carbon atom also ends up with 8 electrons in its valence shell; 4 of its own and 1 from each of the 4 chlorine atoms. However, no electrons are transferred; therefore no ions are formed. The sharing process may be pictured as in Figure 7.10. The bonding that results from this mutual sharing of pairs of electrons is commonly referred to as *covalence,* and the resulting substances are spoken of as *covalent compounds* or *covalent molecules.*

Compounds formed by the combination of two nonmetals are covalent. This is not surprising; since both elements involved have 4 or more valence electrons and therefore have no tendency to transfer electrons, the only way in which they can combine is by mutual sharing of electron pairs.

The binary hydrogen compounds of all nonmetals are covalent. The structures of a number of these compounds are represented in Figure 7.11.



THE NEUTRAL ATOMS COMBINING TO FORM A MOLECULE OF A COMPOUND



THE MOLECULE OF THE COVALENT COMPOUND, CCl_4

Figure 7.10. Formation of a covalent CCl_4 molecule by the mutual sharing of pairs of electrons. Note that the nucleus of each atom is unchanged. Only the electrons of an atom are involved in ordinary chemical reactions.

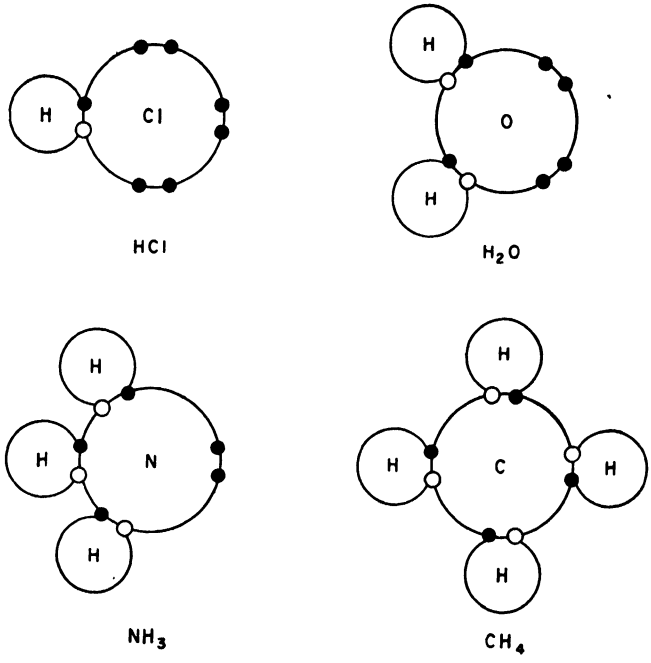


Figure 7.11. Structures of some typical non-metal hydrogen compounds. Note that the hydrogen atom shares a pair of electrons with the non-metal and thereby acquires the electron configuration of the helium atom. The non-metal shares electron pairs with one or more hydrogen atoms and thereby acquires the electron configuration of the nearest inert gas (neon, in the case of oxygen, nitrogen and carbon, and argon, in the case of chlorine). Only the valence electrons are shown in the above structures.

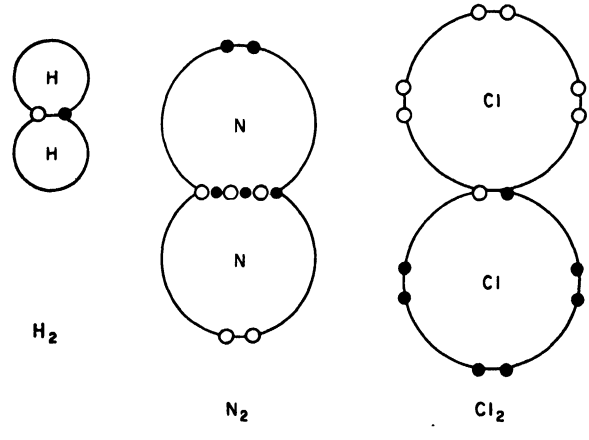
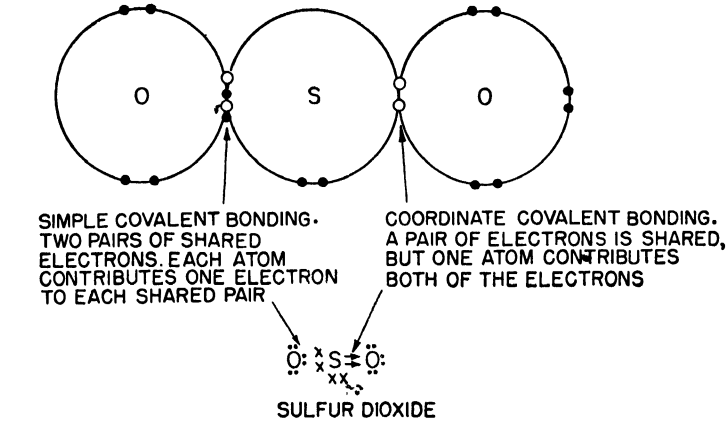


Figure 7.12. Molecules of the diatomic gases H_2, N_2 and Cl_2. ⁻ and O are electrons.

7.9 Molecules of elements. Diatomic molecules of gaseous elements, such as H_2, Cl_2, and N_2, are formed by the mutual sharing of electron pairs in the manner represented in Figure 7.12. Note that 2 nitrogen atoms share 3 pairs of electrons.

7.10 Coordinate covalence. In trying to apply the rule that atoms seek an inert gas structure when they react, it is frequently necessary to assume that the atom of one of the elements can supply both of the



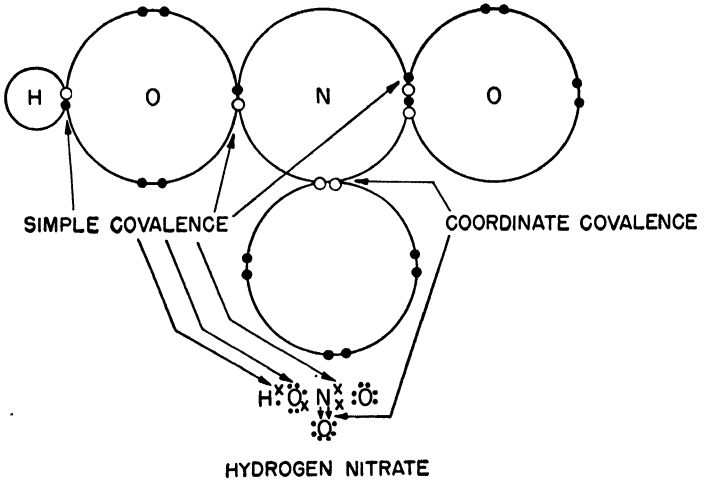


Figure 7.13. Coordinate and simple covalence: two methods of representing the structure of a molecule. The smaller formulation is the one most commonly used. Note that the atoms all attain an inert-gas configuration.

electrons in the mutually shared electron pair. The bond that results from this kind of sharing is called a *coordinate bond*, and the bonding is referred to as *coordinate covalence* or *coordination*. Figure 7.13 illustrates this type of bonding. Simple covalent bonds are represented by dots and crosses. Coordinate bonds are represented by arrows pointing away from the atom that furnishes the shared electrons.

All ternary acids are covalent, and most of them have at least 1 coordinate bond. Since the binary acids all have simple covalent bonding, it follows that *all acids, whether binary or ternary, are covalent.*

It will be found that all ternary and quaternary (4 or more elements) compounds that are made up of only hydrogen and the electronegative elements (the nonmetals) are covalent. This means that *the thousands of organic carbon compounds are covalent.*

In summary it can be said that, as a general rule, *all salts and metal oxides and hydroxides are electrovalent. All other compounds are covalent.*

7.11 Oxidation state and the structure of the atom. Figure 7.14 shows how the oxidation states of the elements are related to their position in the periodic table and, accordingly, to their electronic structure. The following general conclusions can be drawn:

1. The strongly electropositive elements with 1, 2, and 3 valence electrons and a stable electronic structure at subvalence-shell levels transfer these electrons readily, and as a result, generally have only one oxidation number, 1, 2, or 3, depending upon the group in which they fall.

2. Because the transition elements have an unfilled subshell below the valence shell they have variable combining capacity, and hence several oxidation states, even though each has a definite number of valence shell electrons.

3. Because nonmetals can share electrons either by simple covalence or by coordination they generally have several positive oxidation numbers in addition to the negative one which they display in their binary hydrogen compounds and binary salts.

7.12 Polarity of covalent compounds. Although there is no transfer of electrons when a covalent compound is formed, there is, in all except perhaps a few instances, some shift in the position of the shared electrons. Thus when hydrogen and chlorine share a pair of electrons to form the covalent HCl molecule, the positive charges on the nucleus of the highly electronegative chlorine atom attract the valence electron of the hydrogen atom so strongly that it is pulled some distance away from the positive hydrogen nucleus. The net result is that the hydrogen

Figure 7.14

The Oxidation States of the Elements in Relation to Their Positions in the Periodic Table

Period	Orbitals	*s*		*d*										*p* (except He)					Inert gases
	Character	Light metals		Heavy metals										Nonmetals					
	Group	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1	*	H −1, 1																	He
2	*	Li 1	Be 2											B 3	C −4, −2, 2, 4	N −3, −2, −1, 1, 2, 3, 4, 5	O −2, −1	F −1	Ne
3	*	Na 1	Mg 2											Al 3	Si −4, 2, 4	P −3, −2, 1, 3, 4, 5	S −2, 1, 2, 3, 4, 5, 6	Cl −1, 1, 3, 4, 5, 7	A
4	*	K 1	Ca 2	Sc 3	Ti 2, 3, 4	V 2, 3, 4, 5	Cr 2, 3, 6	Mn 2, 3, 4, 6, 7	Fe 2, 3, 6	Co 2, 3, 4	Ni 2, 4	Cu 1, 2	Zn 2	Ga 1, 3	Ge 2, 4	As −3, 2, 3, 5	Se −2, 4, 6	Br −1, 1, 5	Kr
5	*	Rb 1	Sr 2	Y 3	Zr 4	Nb 3, 5	Mo 2, 3, 4, 5, 6	Tc 7	Ru 2, 3, 4, 6, 8	Rh 2, 3, 4	Pd 2, 4	Ag 1	Cd 2	In 1, 2, 3	Sn 2, 4	Sb −3, 3, 4, 5	Te −2, 4, 6	I −1, 1, 3, 4, 5, 7	Xe
6	*	Cs 1	Ba 2	La 3	Hf 4	Ta 5	W 2, 3, 4, 5, 6	Re 3, 4, 5, 6, 7	Os 2, 3, 4, 6, 8	Ir 2, 3, 4	Pt 2, 4	Au 1, 2, 3	Hg 1, 2	Tl 1, 3	Pb 2, 4	Bi −3, 3, 4, 5	Po −2	At −1	Rn
7	*	Fr 1	Ra 2	Ac 3															

* Symbol
Oxidation number
in its compounds

Transition elements

	f orbitals													
Lanthanides Group IIIB	Ce 3, 4	Pr 3, 4	Nd 3	Pm 3	Sm 2, 3	Eu 2, 3	Gd 3	Tb 3, 4	Dy 3	Ho 3	Er 3	Tm 3	Yb 2, 3	Lu 3
Actinides	Th 4	Pa 5	U 3, 4, 5, 6	Np 3, 4, 5, 6	Pu 3, 4, 5, 6	Am 3, 4, 5, 6	Cm 3	Bk 3, 4	Cf 3					

end of the HCl molecule is positively charged, while the chlorine end is negative (see Figure 7.15). The farther an electron is removed from the nucleus of its atom, the stronger the positive charge on that nucleus. Vice versa, the closer a shared electron moves toward a nucleus, the stronger the negative charge on that nucleus. The magnitude of the difference in charge on the two parts of the molecule, and hence the magnitude of the ionic character of the covalent bond, is referred to as the *polarity* of the compound. The ease with which an electron can be pulled away from its normal position in relation to the nucleus of its atom will depend upon: (a) The total charge on the nucleus; the greater the charge the less easily it will be pulled away. (b) The distance from the electron to the nucleus; the greater the distance, the weaker the attractive force and the more easily the electron is pulled away. (c) The number of electron shells that lie between the nucleus and the valence electron; since the electrons in these shells will repel the valence electron, it follows that the greater the number of shells, the more easily the electron will be pulled away. The force with which an electron is attracted to the nucleus of the more electronegative element will likewise be dependent upon the three factors listed above: (a) The greater the charge on the nucleus, the more strongly the electron will be attracted. (b) The shorter the distance from the valence shell to the nucleus, the more strongly the electron will be attracted. (c) The greater the number of intervening electron shells, the greater the repulsion of the electrons in these shells, and hence the less strongly the electron will be attracted.

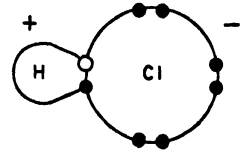


Figure 7.15. Polarity of the covalent HCl molecule.

Electrovalent compounds represent the highest degree of polarity inasmuch as ions are formed by actual transfer of electrons from one atom to another. Among covalent compounds formed by combination of hydrogen with a nonmetal, the ionic character of the covalent bond, and therefore the polarity, increases as the electronegativity of the nonmetal increases. Thus HF is the most strongly polar of these compounds, with H_2O a close second, because fluorine and oxygen are the two most strongly electronegative nonmetals. As with the hydrogen compound, so also with the other nonmetal compounds; the degree of polarity increases as the difference in electronegativity of the constituent elements increases. The most strongly electronegative element is assigned a negative oxidation number; in CS_2 the oxidation number of S is -2, in SO_2 it is $+4$.

A polar covalent molecule is referred to as a *dipole* because its two

ends are oppositively charged. The magnitude of the difference in charge of the two ends of the dipole molecule is referred to by a quantity known as the *dipole moment.*

7.13 The crystal lattices of electrovalent compounds. All salts, metal oxides, and metal hydroxides are electrovalent compounds. Therefore the so-called "molecules" of the solid compound consist of pairs (triplets, quadruplets, etc.) of ions. X-ray examination shows that these ions are the units out of which the crystal lattice of the solid is built. Thus a crystal of NaCl is made up of an orderly arrangement of Na^+ ions, each surrounded by and attached, by electrostatic forces, to 6 Cl^- ions; and Cl^- ions, each surrounded by and attached by electrostatic forces to 6 Na^+ ions. The arrangement can be represented as in Figure 7.16, and is referred to as an *ionic lattice.* Salts are sometimes defined as substances with ionic crystal lattices. This definition would place metal oxides and hydroxides in the salt category.

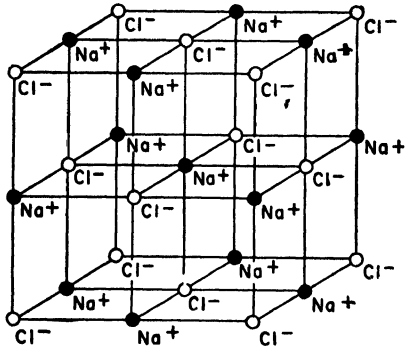


Figure 7.16. The ionic crystal lattice of sodium chloride.

By contrast with electrovalent compounds, covalent compounds have a molecular crystal lattice.

7.14 Melting points of electrovalent and covalent compounds. Because electrovalent compounds have the sort of ionic crystal lattice described in 7.13, the ionic components are all held together by continuous bonds that extend from one ion to another throughout the length and depth of the crystal. As a result the crystal is relatively hard and has a relatively high melting point. By comparison, the covalent compounds are, as a general rule, relatively soft and have relatively low melting points because the molecular components are held together only by surface forces and the attraction of dipoles; there is, as a rule, no continuous bonding. These facts are brought out in Table 7.4, which lists the melting points of representative electrovalent and covalent compounds. In each horizontal row the metal and nonmetal whose compounds are compared are from the same period in the periodic table. The differences in the melting points of the electrovalent metal oxides

TABLE 7.4

MELTING POINTS OF ELECTROVALENT AND COVALENT COMPOUNDS

Electrovalent			Covalent	
Compound	mp, °C		*Compound*	mp, °C
		Oxides		
MgO	2642		SO_2	−72.7
CuO	1026		SeO_2	340
		Chlorides		
NaCl	800		$SiCl_4$	−67.6
$MnCl_2$	650		$AsCl_3$	−16.1
		Bromides		
$MgBr_2$	711		PBr_3	−40
$CaBr_2$	730		$AsBr_3$	51
		Sulfides		
Li_2S	847		CS_2	−110.8
NiS	797		As_2S_3	300

and the covalent nonmetal oxides are brought out in Tables 3.5 and 3.6, pages 85 and 86.

The unique case of SiO_2, which is covalent and has a melting point of 1700°C, emphasizes the fact that covalent molecules can orient themselves so as to give a continuous type bonding, and thereby form extremely stable crystal lattices.

The low melting point of aluminum chloride (190°C at 2.5 atm) suggests that it is not an electrovalent compound. The fact that in the molten state it is not a good electric conductor supports this contention. Because of the position of aluminum along the borderline between metals and nonmetals, the covalent character of its chloride is not surprising.

7.15 Influence of the diameter of the atom on the electropositivity of the metal. If the common metals listed in Table 3.3 are arranged, in the periodic groups in which they fall, in the order of their increasing electropositivities, the arrangement given in Table 7.5 is obtained.

For the strongly electropositive (highly reactive) metals in groups IA and IIA, the greater the atomic diameter, the greater the electropositivity. However, in the case of the metals in groups IB and IIB the electropositivity decreases as the diameter increases. The electropositivity (reactivity) of a metal is determined by the ease with which its valence electrons are given off to form the positive charge on the nucleus. According to a fundamental law of electrostatics the force of attraction

TABLE 7.5

RELATION BETWEEN ELECTROPOSITIVITY AND ATOMIC DIAMETER OF SOME COMMON METALS

Group	IA		IIA		IIIB		IB		IIB		IIIA		IVA	
Order of increasing electropositivity ↓	At. diam.		At. diam.		At. diam.		At. diam.		At. diam.		At. diam.		At. diam.	
	Na	0.98	Be	0.34	Sc	0.83	Au	1.37	Hg	1.12	In	0.92	Pb	1.32
	K	1.33	Mg	0.78	Y	1.06	Ag	1.13	Cd	1.03	Ga	0.63	Sn	0.74
	Rb	1.49	Ca	1.06	La	1.22	Cu	0.96	Zn	0.83	Al	0.57		
	Cs	1.65	Sn	1.27										
	Li	0.78	Ba	1.52										

between two oppositely charged bodies is directly proportional to the product of the charges and inversely proportional to the square of the distance between them. As the atomic number of an element in a group increases, the positive charge on the nucleus increases. This will increase the force of attraction between the valence electron and the nucleus and will decrease the electropositivity. As the atomic number increases, the radius of the atom increases; this will have a pronounced decreasing effect on the force of attraction, and will accordingly increase the electropositivity. The net ease with which electrons are given off will be the resultant of the charge on the nucleus, the radius of the atom, and other factors which can be grouped together as specific effects. In the case of the group IA and IIA metals (lithium excepted) the radius of the atom appears to be the dominant factor. We can say in the case of these metals that as the diameter increases, the valence electron (or electrons), being farther away from the nucleus, is more weakly bound and is therefore more easily removed. The net result is that, for the metals of groups IA and IIA, as the diameter of the atoms in the group increases, the reactivity (electropositivity) of the metal increases. In the case of the group IB and IIB metals, the effect of increase of radius is apparently overshadowed by the combined effect of specific factors and increase in charge on the nucleus. As a result, as the diameter increases the reactivity decreases.

7.16 Influence of the diameter of the atom on the electronegativity of the nonmetal. The nonmetals form binary compounds by drawing electrons into their valence shells, either by transfer or by

sharing. The attractive force is furnished by the positive charge on the nucleus. Therefore the greater the radius of the atom, the less the force with which electrons are attracted and the lower the electronegativity (reactivity). The increase in the charge on the nucleus as the atomic number increases should increase the force of attraction. This, however, is nullified by the fact that the increased number of electrons as the atomic number increases causes the foreign electrons to be repelled with increased force. The dominant factors are therefore diameter and specific factors. The experimentally determined order of electronegativity of the nonmetals in each group is given in Table 7.6. In each

TABLE 7.6

RELATION BETWEEN ELECTRONEGATIVITY AND ATOMIC DIAMETER OF THE NONMETALS

Group	IVA		VA		VIA		VIIA	
Order of increasing ↑ electronegativity	El.	At. diam.	El.	At. diam.	El.	At. diam.	El.	At. diam.
	C	1.54	N	1.48	O	1.48	F	1.44
	Si	2.35	P	2.20	S	2.08	Cl	1.99
	Ge	2.45	As	2.42	Se	2.34	Br	2.28
	Sn	2.82	Sb	2.82	Te	2.74	I	2.67
	Pb	3.08	Bi	3.04				

instance the electronegativity of the nonmetal decreases as the diameter of the atom increases. Since electropositivity is a characteristic of metals, while electronegativity is a characteristic of nonmetals, we can conclude from the data in Tables 7.5 and 7.6 that in the A groups, as the atomic number increases the element becomes less nonmetallic and more metallic.

7.17 Influence of the position of an element in a period on its electronegativity. Attention has already been called to the fact that the metals fall to the left and below the zigzag diagonal line in the periodic table, while the nonmetals fall above and to the right of this line. Furthermore, we have noted that the most strongly electropositive elements fall in groups IA and IIA, while the most strongly electronegative element, fluorine, falls in group VIIA. In the data given in Table 7.7, in which the metals in the period are arranged from left to

TABLE 7.7

ORDER OF ELECTROPOSITIVITIES AND ELECTRONEGATIVITIES OF THE ELEMENTS IN A PERIOD

B group elements are in **boldface** type.

Period	Order of decreasing electropositivities ⟶	Order of increasing electronegativities ⟶
2	Li Be	B C N O F
3	Na Mg	Al Si P S Cl
4	K Ca **Sc Ti Mn V Zn Cr Ga Fe Co Ni Cu**	Ge As Se Br
5	Rb Sr **Y Zr Cd** In **Mo** Sn **Ag Pd**	Sb Te I
6	Cs Ba **La Hf** Tl Pb **Hg Au**	

right in the order of their decreasing electropositivity, and the nonmetals are arranged in the order of increasing electronegativity, we can conclude that for the A groups as the atomic number increases in a period, that is, as you move from left to right, the electropositivity decreases and the electronegativity increases. If we confine ourselves to the A groups and overlook lithium, we find that as the atomic number increases in going from left to right, the atomic diameter decreases in regular order (see Figure 7.7). Therefore it is experimentally true that, for the A groups, as the diameter of the atom in a period decreases, its electropositivity decreases and its electronegativity increases. This is in complete accord with the change that has already been noted within each A group (see Sections 7.15 and 7.16).

7.18 Relation between the stability of a binary compound and the electropositivity of its constituent elements. The least stable oxides, PtO_2, Au_2O_3, Ag_2O, and HgO are derived from the least electropositive metals; in contrast the strongly electropositive metals form very stable oxides. This illustrates the general rule that the stability of the binary compounds increases as the electropositivity of the metal increases. Likewise, the stability of the binary compounds of the nonmetals increases as the electronegativity of the nonmetal increases. To illustrate, HI is so unstable that it can be decomposed by moderate heating. The decomposition temperature increases from HI to HBr to HCl to HF. Recalling what has been stated in Sections 7.15, 7.16, and 7.17 about the relationship between the position of an element in

the periodic table and its electropositivity or electronegativity, it follows that:

1. In any period the stability of the binary compound formed by each nonmetal of the period with a specific metal increases as the atomic number of the nonmetal increases. Thus $CaCl_2 > CaS > Ca_3P_2$.

2. In any group the stability of the binary compound formed by each nonmetal of the group with a specific metal increases as the atomic number of the nonmetal decreases. Thus $MgO > MgS > MgSe > MgTe$.

3. In groups IA and IIA the stability of the binary compounds formed by each metal in the group with a specific nonmetal increases as the atomic number of the metal increases. Thus $CsCl > RbCl > KCl > NaCl$.

4. In the B groups the stabilities of the binary compounds formed by each metal in the group with a specific nonmetal tend to decrease as the atomic number of the metal increases. There are many exceptions to this rule. This is in line with the irregular behavior displayed by the B group elements. Most of the unusual behavior of these elements is probably associated with the fact that their structures have incomplete subshells.

7.19 Conductivity of metals. Metals, as a general rule, have 4 or fewer valence electrons. The fact that metals form positive ions, and hence are electropositive, shows that these electrons are not firmly bound to the atom. Because they are not firmly bound they are free to move from one atom to another; it is as if an electron is not firmly bound to a specific atom but is the common property of all the atoms in the piece of metal. As a result of this free movement of electrons, the metal is a good conductor of electricity. *Electric current* is simply the movement of electrons.

Heat is conducted by being passed from atom to atom by way of the electrons. The freedom of movement of the electrons means that heat passes readily, that is, the metal is a good conductor of heat.

The electrons of nonmetals are not mobile or readily transferable. Therefore the nonmetals are not good conductors.

Questions and Problems

1. Define or describe each of the following: electron; neutron; proton; atomic number; nucleus; valence electrons; transfer of electrons; electrovalence; ion; positive ion; negative ion; ionization; electropositive element; electronegative element; sharing of electrons; polar compound; dipole; nonpolar compound; covalence; coordinate co-

valence; coordination; electron pair; metals; nonmetals; transition elements; inert gases; isotopes; ionic lattice; salts.

2. Why is sodium classed as a metal, while chlorine is classed as a nonmetal? Account for the difference between sodium and chlorine on the basis of their atomic structures.

3. On the basis of their structures account for the fact that sodium is a less reactive metal than potassium.

4. On the basis of their structures account for the fact that sodium is a more reactive metal than magnesium, which in turn is more reactive than aluminum.

5. On the basis of their structures account for the fact that fluorine is more reactive than chlorine and also more reactive than oxygen.

6. Account for the fact that argon, helium, neon, and xenon are inert.

7. How can you determine whether a compound is electrovalent or covalent?

8. How would you account for the fact that indium, which has 3 valence electrons, is metallic in character, while boron, which has 3 valence electrons, is distinctly nonmetallic?

9. Elements w, x, y, and z have atomic weights of 28, 40, 24, and 37, respectively, and atomic numbers of 14, 18, 12, and 17, respectively. Which of these elements is a metal? Which is a nonmetal? Which is an inert element? Give the valences of each and indicate whether they would be expected to form electrovalent or covalent compounds. Sketch the simple electronic configuration of each atom and show also the number of protons and neutrons in each nucleus.

10. The following pure liquids are nonconductors: H_2O, SO_2, NH_3, CCl_4. Sketch the molecule of each, showing the disposition of all valence electrons.

11. The following melted compounds are conductors: NaCl; MgF_2; $AlBr_3$; ZnO. Sketch the structure of each showing the disposition of all valence electrons.

12. An element has an atomic weight of 24 and an atomic number of 11. In what periodic group does it fall? What is its valence? Is it a metal or a nonmetal?

13. Which is more metallic, arsenic, or bismuth? Tin or lead? Explain.

14. Which is more stable, $CaCl_2$ or $MgCl_2$? $CaCl_2$ or CaF_2? H_2S or H_2Te? KF or CuS? Explain.

15. Which is the more dense solid, arsenic or antimony? Strontium or zirconium? Calcium or barium? Explain.

16. Which is more reactive, chlorine or bromine? Barium or magnesium? Explain.

17. Which has the greater diameter, Na^+ or Al^{+++}? S^{--} or F^-? K or Ca? Cs or Li? Ba or Ba^{++}? S or S^{--}? Explain.

18. Which is more electropositive, Sr or Be? Na or Rb? Ca or Ge? Ag or Cu? Zn or Br? Explain.

19. Which has the higher melting point, $CaCl_2$ or $AsCl_3$? MgO or SO_2? H_2Se or CaSe? Explain.

20. Which is more electronegative, Cl or I? S or Cl? N or As? O or P? As or F? Explain.

21. Which is the better conductor of electricity, Na or S? Si or Cu? Liquid KCl or liquid PCl_3? Water or melted Na_2O? Explain.

22. Which is the better conductor of heat, Cr or Se? S or Ag? Explain.

23. What relationships exist between the following? (a) The atomic numbers and atomic diameters of the elements in a group. (b) The atomic numbers and atomic diameters of the elements in a period. (c) The atomic numbers and electropositivities of the metals in an A group. (d) The atomic numbers and electronegativities of the nonmetals in an A group. (e) The atomic numbers and electronegativities of the nonmetals in a period. (f) The atomic numbers and electropositivities of the metals in a period. (g) The electronegativity of a nonmetal and the stability of its binary compound with a metal. (h) The electropositivity of a metal and the stability of its binary compound with a nonmetal. (i) The diameter of the atom of a metal in a periodic group and its electropositivity. (j) The diameter of the atom of a nonmetal in a periodic group and its electronegativity. (k) The diameter of an atom and the diameter of its simple ion. (l) The density of an element and its position in a periodic group. (m) The stability of a binary compound and the position of its constituent elements in the periodic table. (n) The density of an element and its position in a period. (o) The melting point of a compound and the bonding of its constituent elements.

24. Pure, dry, liquid H_3PO_4 does not conduct electricity. Experiments prove that, in the molecule of H_3PO_4, hydrogen atoms are at-

tached to oxygen atoms but are not attached to atoms of P, that the atoms of O are attached to H and P but are not attached to each other. Sketch the molecule of H_3PO_4. Designate, by name or by conventional notation, each valence bond.

25. What relationships exist between the following? (a) The periodic group in which an element falls and the number of *s* electrons in its valence shell. (b) The periodic group in which an element falls and the number of *p* electrons in its valence shell. (c) The periodic group in which an element falls and the number of *d* electrons in its electronic configuration. (d) The periodic group in which an element falls and the number of *f* electrons in its electronic configuration.

26. Show the detailed orbital arrangement of all electrons in the following atoms: Be; Si; Se; Sb; Rn; Pd; Ho; Pu.

CHAPTER 8

The Nucleus of the Atom

Note to instructor: Discussion of this chapter can be postponed without interfering with the logical development of the subject matter in this book.

8.1 Nuclear changes. In the discussion of the structure of the atom in Chapter 7 very little reference was made to the nucleus except to state that it contained all the protons and neutrons, and represented therefore practically the entire mass of the atom. Attention was called to the fact that the isotopes of an element differ only in the number of neutrons in the nucleus. The electrons that make up the structure are all arranged in a definite pattern outside the nucleus, and the chemical properties of an element are determined by the number and arrangement of these electrons. Chemical combination of elements to form compounds involves a transfer or sharing of certain of these electrons; in ordinary chemical reaction, therefore, no change whatever takes place in the nucleus.

Changes in the nucleus of atoms do take place, however; some of them go on naturally and spontaneously, others can be induced in the laboratory. These changes are

1. *Natural radioactivity*
2. *Transmutation of elements by nuclear bombardment*
3. *Radioactive decay of radioelements*
4. *Nuclear fission*
5. *Nuclear fusion*

8.2 Natural radioactivity. The nuclei of atoms of all naturally occurring elements with atomic numbers higher than 82, except Bi^{209}, are unstable. As a result these nuclei undergo slow decay. This decay involves loss of either an electron (called a *beta* particle and designated by the Greek letter beta (β) and represented by the notation $_{-1}e^{0}$) or a helium ion (called an *alpha* particle and designated by the Greek letter alpha (α) and represented by the notation $_{2}He^{4}$. In this standard notation the subscript, placed before the symbol, denotes the atomic number, while the superscript, placed after the symbol, denotes the mass number of the nuclide). The decay process is called *radioactivity*, *radioactive*

disintegration, or *radioactive decay*, and the element is said to be *radioactive.*

The alpha particle has a mass of 4 and carries 2 positive charges; the ejection of such a particle means that the mass of the atom has decreased by 4 mass units and the charge on the nucleus (the atomic number of the element) has decreased by 2 positive units. In other words, a new element is produced whose mass number is 4 less than that of the parent element and whose atomic number is 2 less.

A beta particle, being an electron, has a charge of -1 but has practically zero mass. Therefore its loss produces no change in the mass number of the parent element. The loss of an electron from a nucleus which presumably contains no electrons can be accounted for by assuming that it is formed from a neutron by the process indicated by the reaction

$$\text{neutron} - \text{electron} = \text{proton} + \text{energy}$$

This agrees with the concept that neutrons and protons have approximately the same mass. The mass and charge relationship in the reaction are shown if we use conventional symbols in the above reaction, ${}_0n^1$ for neutron, ${}_{-1}e^0$ for electron and ${}_1\mathrm{H}^1$ for proton.

$${}_0n^1 - {}_{-1}e^0 = {}_1\mathrm{H}^1$$

The loss of a beta particle means therefore that the atomic number has increased by 1. That means that a new element has been produced whose mass number is the same as that of the parent element but whose atomic number is one unit higher.

To illustrate, uranium (U^{238}) decays with the emission of an alpha particle, while thorium (Th^{234}) emits a beta particle. The decay reactions, represented by the use of conventional symbols, would be

(1) ${}_{92}\mathrm{U}^{238} = {}_{90}\mathrm{Th}^{234} + {}_2\mathrm{He}^4$ (alpha particle emitted)

(2) ${}_{90}\mathrm{Th}^{234} = {}_{91}\mathrm{Pa}^{234} + {}_{-1}e^0$ (beta particle emitted)

It should be noted that in each of these decay reactions, the sum of the mass numbers of the products equals the mass number of the parent atom and the algebraic sum of the charges of the products equals the charge on the nucleus of the parent. Thus $\mathrm{Th}^{234} + \mathrm{He}^4 = \mathrm{U}^{238}$ and ${}_{90}\mathrm{Th} + {}_2\mathrm{He} = {}_{92}\mathrm{U}$. Likewise, $\mathrm{Pa}^{234} + e^0 = \mathrm{Th}^{234}$, and ${}_{+91}\mathrm{Pa} + {}_{-1}e = {}_{+90}\mathrm{Th}$.

Additional decay reactions are given in Section 8.6.

The escape of either alpha or beta particles is accompanied in many, but not all, cases by the emission of *gamma radiation.* Gamma rays are very short x rays and are designated by the Greek letter gamma (γ) (see Figure 8.1).

It should be emphasized that radioactive decay of an atom involves loss of *either* an alpha particle *or* a beta particle; both particles are never lost from the same nucleus at the same time. Normally, a nucleus always decays by the loss of the same particle, either an α or a β. In a few cases, ${}_{83}Bi^{214}$ for example, a nucleus can undergo both α decay and β decay; not, however, in the same step, from the same atom.

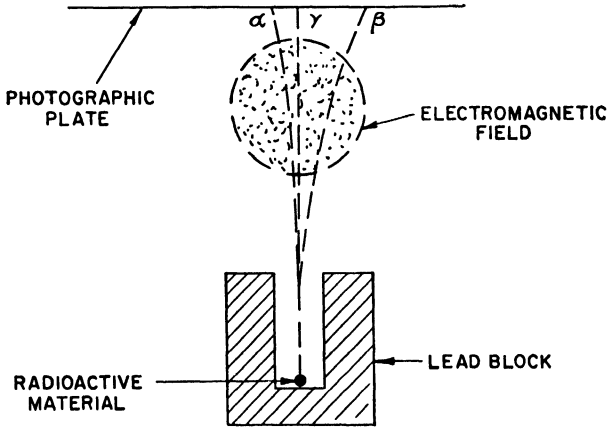


Figure 8.1. Proof of the identity of radioactive rays. When the rays which are emitted by a radioactive substance are passed through a magnetic field they are deflected in such a way as to prove that the alpha rays are positively charged, the beta rays are negatively charged and the gamma rays are neutral. From the extent to which each ray is deflected it can be calculated that the beta particle is about 1/1850 as heavy as the hydrogen atom while the alpha particle has the same mass as the helium atom. The gamma ray has no mass and is, in effect, an x ray. The radioactive rays do not pass through a lead block.

To compensate for the 2 protons that are lost when an alpha particle escapes from a nucleus, 2 electrons spontaneously escape from the electron shells of the atom and restore it to a condition where the number of protons equals the number of electrons. These escaping electrons pass into the surrounding atmosphere. The alpha particle which has been ejected into the atmosphere, being a helium ion with 2 positive charges, picks up 2 electrons from the atmosphere and becomes an atom of helium gas. The over-all result is that the electrons that are lost in one process are gained in another process.

When a beta particle (${}_{-1}e^{0}$) escapes from a nucleus into the atmosphere as a result of the reaction

$$\text{neutron} - \text{electron} = \text{proton}$$

the number of positive charges on the nucleus is increased by 1. To compensate for this increase, an electron from the atmosphere slips into one of the electron shells and restores the atom to a state of neutrality. Here again the electron that is lost in one process is gained in another.

8.3 Penetrating power of radioactive rays. Alpha, beta, and gamma particles are all ejected at high speeds. Alpha particles are emitted at speeds ranging from 9000 to 14,000 miles/sec. Beta particles are commonly ejected at speeds of from 60,000 to 100,000 miles/sec; in rare cases, the speed may run as high as 180,000 miles/sec. All gamma rays travel at the speed of light, 186,000 miles/sec. The alpha or beta particles from a specific nucleus are not all ejected at the same speed.

The ability of a particle to penetrate material is a function of its speed. In line with this fact, gamma rays are the most penetrating and alphas the least, the relative penetrating power of the three being in the approximate order of 10,000 for γ to 100 for β to 1 for α. Alpha rays will not penetrate an ordinary sheet of paper or thin glass. Beta rays will penetrate thin glass but are stopped by thin sheets of metal, for example, by a $\frac{1}{16}$-inch sheet of aluminum. Gamma rays will pass through great thicknesses of wood, glass, or flesh, and can even penetrate 9 or 10 in. of lead.

8.4 Detection of radioactive rays. The alpha, beta, and gamma rays can be detected by the fact that, either individually or collectively, they will produce the following effects:

1. *A Geiger-Mueller type counter will be actuated.* The essential part of this counter (see Figure 8.2) is a partially evacuated tube with a pair of sealed-in electrodes across which is applied a voltage just insufficient to allow current to flow. When radioactive rays enter the counter tube, the conductivity of the gas which it contains is increased, either as a result of the entrance of electrons (β rays) or because of ionization of the

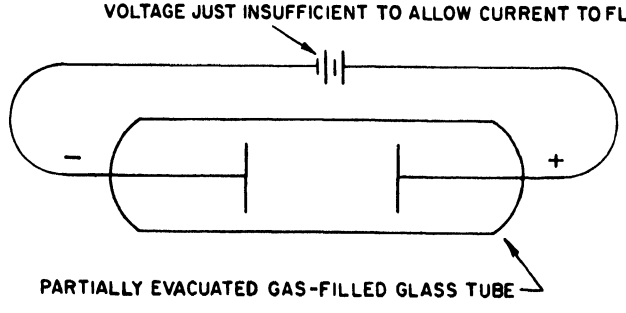


Figure 8.2. Geiger-Mueller type counter.

gas by the entering rays. As a consequence of this increased conductivity, current will pass through the tube and through the circuit and will cause a light to flash and a counting device to operate. The instrument can be adjusted so that each entering particle will cause one count to be registered; not only will the counter *detect* radioactive rays but it will *measure* the rate at which they are being given off. Since, for any radioactive material, the rate of decay is directly proportional to the concentration of the radioactive species, the counter provides an excellent means for determining this concentration.

By constructing the counter tube of glass of the correct thickness, filling it with vapor of the correct ionizability, and otherwise adjusting the system, a counter can be made which will detect only gamma rays, only beta rays, only gamma and beta rays, or all three rays. Also, a tube that will detect only one ray can be adjusted so that it will select only those rays which lie within a certain range of intensity. In this way a mixture of emanations from a mixture of radioactive species can be resolved into its several components.

2. *A charged electroscope will be discharged:* The rays ionize the air around the electroscope (see Figure 8.3) and cause it to become a conductor. As a result the charge on the electroscope is conducted away.

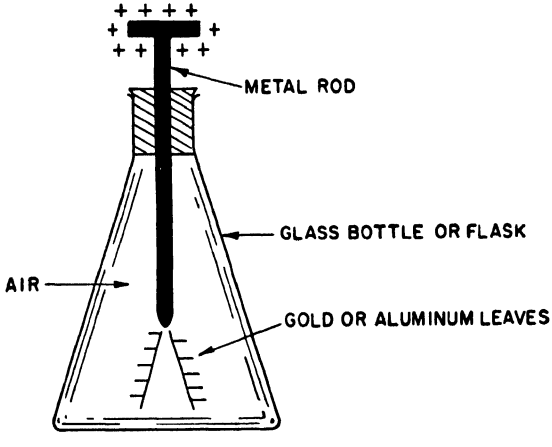


Figure 8.3. A charged electroscope.

3. *An unexposed photographic plate will be affected.* The black paper in which photographic plates and films are wrapped will keep out light but will not keep out gamma rays. These rays will affect the silver halide which is the active component of a photographic plate in much the same manner that the halide is affected by light. That means that a wrapped plate will become fogged if it is left in contact with radioactive

material (see Figure 8.4). It is of interest to note that it was such fogging of a photographic plate by a sample of the uranium ore *pitchblende* (U_3O_8) which led to the discovery of radioactivity by Becquerel in 1895.

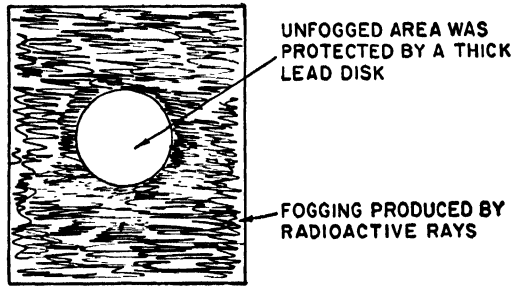


Figure 8.4. Fogging of a photographic plate by radioactive rays. The photographic plate, in its light-protecting wrapping, was placed on the desk top. A lead disk was then placed on top of the plate and a piece of pitchblende (U_3O_8) was then placed on top of the disk and allowed to remain for an hour. When the plate was developed the result represented in the figure was obtained. Radioactive rays had penetrated the wrapping but had not penetrated the lead.

4. *Certain salts will be caused to fluoresce.* When the rays fall upon certain compounds, notably zinc sulfide (ZnS), these solid compounds glow, because of emission of visible light rays. This reaction is the basis for the use of a mixture of zinc sulfide and a radium salt for coating the luminous parts of watches, clocks, and other instruments.

5. *Fog tracks will be generated in a cloud chamber.* A cloud chamber is a small box of some sort containing air saturated with the vapor of some liquid. When a moving particle that can cause ionization of a gas, an alpha or beta particle for example, passes through the air in the chamber, the vapor of the liquid condenses on the ions that are produced. As a result a fog track forms in the wake of the moving particle. The generation of such fog tracks is evidence that a substance being investigated is radioactive.

The Geiger-Mueller type counter is more sensitive than the other four means of detection listed above.

8.5 Rate of decay of a radioactive element. With the aid of the Geiger-Mueller type counter it is possible to determine what kind of a ray is given off (α or β) when a radioactive element decays, the intensity of that radiation, and the rate at which it is emitted. This rate is expressed in a unit called the *half-life. The half-life of a substance is the length of time required for one-half of any given quantity of the substance to*

decay. Radium decays according to the reaction

$$_{88}\mathrm{Ra}^{226} = {}_{86}\mathrm{Rn}^{222} + \text{alpha particle } ({}_{2}\mathrm{He}^{4})$$

Its half-life is about 1620 years. That means that if we were to set aside 1 gram of pure radium today, $\frac{1}{2}$ gram would remain 1620 years from now. One-quarter gram would remain 3240 years from now, and $\frac{1}{8}$ gram would remain 4860 years from now.

It is customary, in writing the equation showing disintegration of a substance, to indicate its half-life in years (y), days (d), hours (h), minutes (m), or seconds (s). Thus for the decay of radon the equation would be

$$_{86}\mathrm{Rn}^{222} \xrightarrow[3.825\ \mathrm{d}]{\alpha} {}_{84}\mathrm{Po}^{218}$$

This means that radon decays with the emission of an alpha particle to give the polonium isotope whose atomic number is 84 and whose mass number is 218. The half-life of radon is 3.825 days. If the alpha or beta ray is accompanied by a gamma emission that fact is generally represented as shown in the following example.

$$_{90}\mathrm{Th}^{230} \xrightarrow[8.3 \times 10^{4}\ \mathrm{y}]{\alpha,\ \gamma} {}_{88}\mathrm{Ra}^{226}$$

As far as can be determined, the rate of radioactive decay is independent of the temperature.

It should be pointed out that the radioactivity of an element is not affected to any considerable extent by the chemical state in which it exists. Radium decays at the same rate and yields the same products whether it exists as the free element, the chloride, the oxide, or the bromide; whether it is in solution, in the solid state, or in the state of a vapor. Furthermore, the chemical properties of a radioactive element are independent of and unaffected by its radioactive behavior. Thus radium reacts with cold water to yield $Ra(OH)_2$ and H_2, just as do Ba, Sr, and Ca. The water solution of $Ra(OH)_2$ is strongly alkaline, just as are $Ba(OH)_2$, $Sr(OH)_2$, and $Ca(OH)_2$. This independence of the chemical and radioactive properties of an element supports the concept, contained in the theory of the structure of the atom, that the chemical properties of an element are determined entirely by the number and arrangement of its electrons and are not affected by the nucleus. It supports, further, the concept that radioactive decay is a property of the nucleus only and does not involve the electrons, which, according to the theory, lie outside the nucleus. The escape of helium ions (alpha particles) from the nucleus, the decrease of 2 in the atomic number when an alpha particle is ejected, the escape of electrons (beta particles) from the nucleus, the

increase of 1 in the atomic number when a beta particle escapes, and the conversion of an alpha particle to an atom of helium gas when it comes in contact with the free electrons in the atmosphere all give additional support to the modern theory of the structure of the atom.

8.6 The disintegration series. Not only is uranium, $_{92}U^{238}$, radioactive, but its daughter (the new element formed when it decays),

FIGURE 8.5

THE URANIUM 238 DISINTEGRATION SERIES

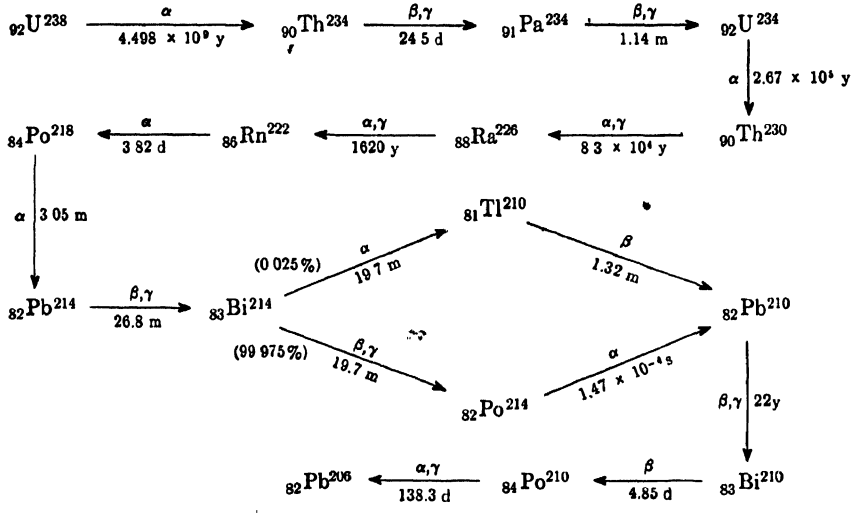
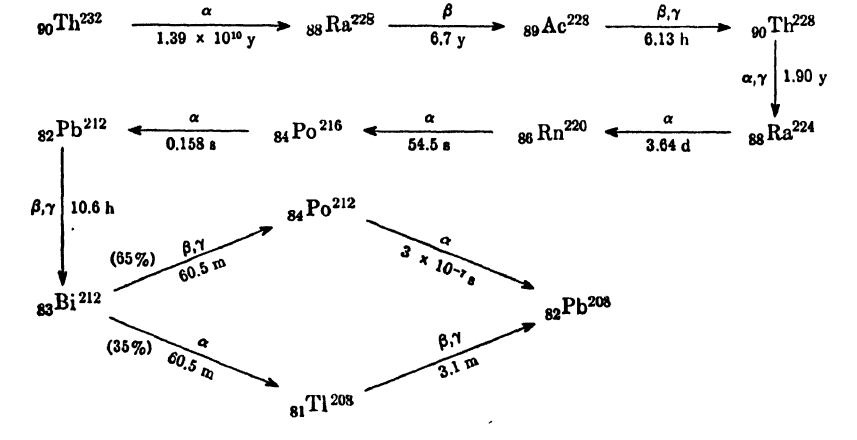


FIGURE 8.6

THE THORIUM 232 DISINTEGRATION SERIES



grand-daughter, great-grand-daughter, and so on down to the fifteenth generation ($_{84}Po^{210}$) are also radioactive. When a piece of uranium starts to disintegrate, the process continues right down the series until the end product, $_{82}Pb^{206}$, is reached. Figure 8.5 represents the reaction that takes place in each step, the half-life of the reaction, and the atomic number, symbol, and mass number of the isotope formed. The atomic number will locate the position of each element in the periodic table. Figure 8.6 represents the thorium-232 series. Similar series can be represented for U^{235} (commonly referred to as the actinium series) and Np^{237}.

8.7 Some practical aspects of radioactivity. 1. *Use of radium and radon in medical therapy.* Radium and radon have long been used for the treatment of cancer. This use depends on the therapeutic effect of the alpha, beta, and gamma rays, and this effect in turn stems from the fact that these rays have energy. One can picture this therapy as being the result of a bombardment of the cancerous area by a barrage of projectiles which eventually destroy it. The radioactive rays will destroy healthy tissue too; this is particularly true of the gamma radiation, which is the most penetrating of the three rays. That is why the patient and the doctor must both be protected by lead shielding.

2. *Manufacture of luminous enamels.* The use of a mixture of zinc sulfide and minute quantities of a radium salt in the making of luminous enamels for watch and clock dials has already been mentioned in Section 8.4.

3. *Calculation of the age of the earth.* The uranium disintegration series (Figure 8.5) shows that lead is the end product of the disintegration. It accounts, therefore, for the fact that all uranium ores contain lead, and enables us to calculate how long it would take the per cent of lead that is present in a uranium ore to accumulate. The calculation is made approximately as follows: First, determine the exact weight of lead and uranium in a definite weight of ore. Second, calculate how much uranium must have decayed in order to yield this exact weight of lead. The sum of this calculated weight and the weight of uranium now present gives the weight of the pure uranium originally present and enables us to calculate what per cent of the original uranium has decayed. Since we know that half of the uranium will decay in 4.5 billion years, we can then calculate from a standard radioactive half-life curve how many years would have been required for the calculated per cent to decay. Assuming that the pure uranium was deposited when the mineral was first formed, we then have made a fairly accurate calculation of its age. The age of the earth, according to such calculations, is about 4.6 billion years.

8.8 Transmutation of elements by nuclear bombardment. The present concept of the structure of the atom postulates that:

1. The nucleus of the atom is made up of neutrons and protons.
2. All neutrons and protons are contained in the nucleus of the atom.
3. The atomic number of an element, and hence its identity as a specific element, is determined by the number of protons.
4. The isotopes of an element differ only in the number of neutrons in their nuclei.

If these postulates are true, it should be possible to *transmute* one element to another by bombarding the nucleus of its atom with protons, neutrons, or alpha particles. To make a long story short, that can be done. A majority of the elements in the periodic table have been transmuted into other elements. The method used is essentially simple; a mass of the pure element or a convenient compound is bombarded for a length of time with the appropriate projectile "particle." Analysis of the product determines whether or not a transmutation has been effected and identifies the new element produced.

8.9 The bombarding particles. Table 8.1 lists the particles which are commonly used as projectiles in transmutation and gives the common source of each.

TABLE 8.1

PROJECTILES FOR NUCLEAR TRANSMUTATION

Name	*Symbol*	*Source*
Neutron	${}_0n^1$	(1) Fission of U^{235} and Pu^{239} in the nuclear reactor (2) Bombardment of ${}_4Be^9$ by alpha particles from the decay of radium ${}_4Be^4 + {}_2He^4 = {}_6C^{12} + {}_0n^1$
Alpha particle	${}_2He^4$	(1) Radioactive decay of radium (2) Helium ions accelerated by the cyclotron (Figure 8.7)
Proton	${}_1H^1$	Protons (gaseous hydrogen ions) accelerated by the cyclotron or the van de Graaff generator (Figure 8.8) or linear accelerator (Figure 8.9)
Deuteron	${}_1D^2$	Deuterons (gaseous deuterium ions) accelerated by the cyclotron, van de Graaff generator, or linear accelerator
Gamma rays (x rays)		High-voltage x-ray machines

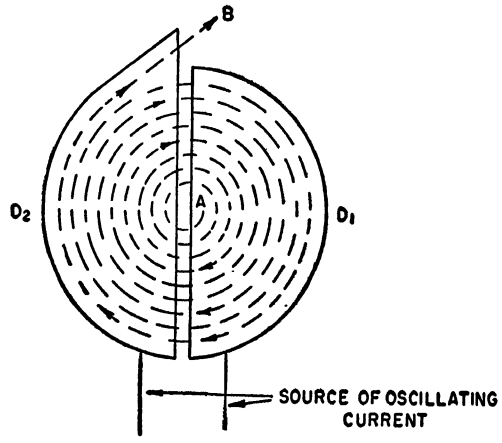


Figure 8.7. The principle of the cyclotron. The charged projectile (a proton, H^+, for example) is introduced at A. The charges on D_1 and D_2 are such that the proton is repelled by D_1 and attracted by D_2. As a result, it begins to move along the path represented by the dashed line. The oscillations of the current are timed so that when the particle crosses the gap between the two D's the charge on each D is reversed. As a result the proton is continually being pushed by one D and pulled by the other. This causes it to move faster and faster. When it finally emerges at B and strikes the material being bombarded it is traveling at a very high velocity and has very high energy.

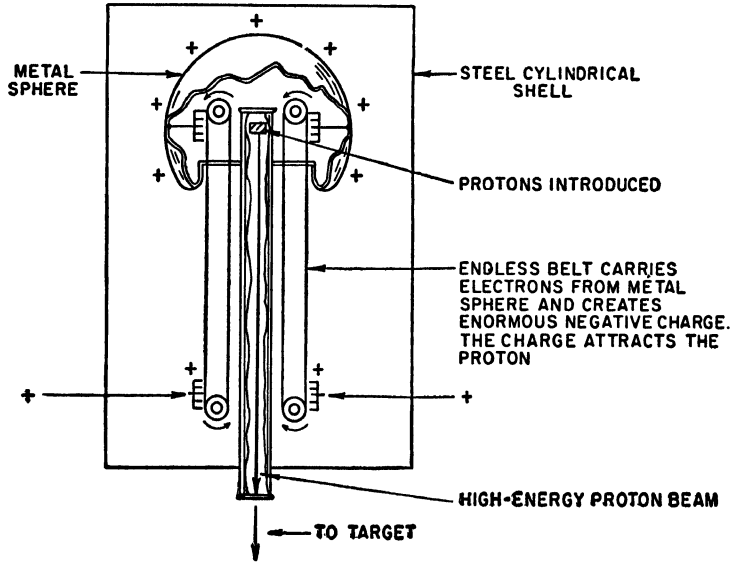


Figure 8.8. The van de Graaff generator. A large difference of potential is built up between the point at which the charged projectile is introduced and the point where it is ejected. As a result it is pushed and pulled with such terrific force that it acquires enormous velocity and energy.

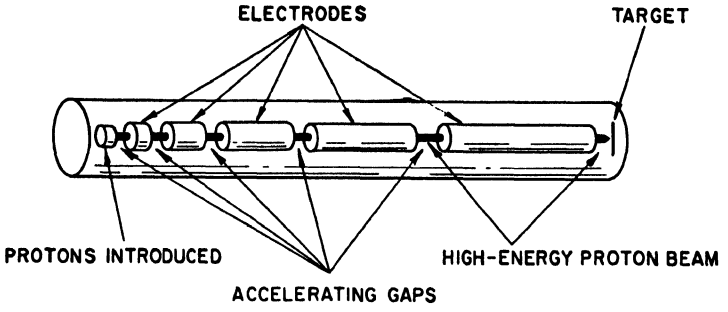


Figure 8.9. The linear accelerator. The principle of its operation is similar to that of the cyclotron except that the electrodes are arranged in a straight line. The oscillating current reverses the charge on the electrodes at such intervals that the particle is pushed and pulled forward at ever-increasing velocity and energy.

8.10 Some typical transmutations. The following equations represent a few typical transmutations. The extended form of the equation is given at the left, with the abbreviated form at the right. It will be noted that, in the abbreviated form, the order of arrangement is: target element, bombarding particle, ejected particle, product element. Thus the notation ${}^{9}_{4}\mathrm{Be}(\alpha,n){}^{12}_{6}\mathrm{C}$ means: beryllium, with mass number of 9 and atomic number of 4 is bombarded with an alpha particle; carbon, with mass number of 12 and atomic number of 6, is formed as a product, and 1 neutron is ejected in the process.

Authors differ as to the notation used when designating the atomic number and mass number of an element. The most common usage appears to be ${}_{92}\mathrm{U}^{238}$ and ${}_{7}\mathrm{N}^{14}$, where 92 and 7 are the atomic numbers and 238 and 14 are the mass numbers, but a number of authors favor the notation ${}^{238}_{92}\mathrm{U}$ and ${}^{14}_{7}\mathrm{N}$. To prepare the student better for future reading, both notations are used below.

In all transmutations the projectile particle is captured and some other particle is ejected. The examples have been selected so that, for a given bombarding particle, the ejected particle is different in each example. In a few instances 1 projectile particle is captured and 2 of the same particles are ejected. The difference in the effect of the same bombarding particle on the same nucleus, as shown in equations (4) and (6) and also in equations (9) and (11), is mainly the result of difference in energy (speed) of the particle.

The same balance of mass numbers and charges must be maintained in equations for transmutation reactions as in equations for radioactive decay processes; the sum of the mass numbers of the reactants must

equal the sum of the mass numbers of the products and the algebraic sum of the charges must be equal.

Although the equations given below do not mention energy of reaction, it should be pointed out that very large amounts of heat are, as a rule, involved in all transmutations. Whereas heats of reaction in ordinary chemical reactions rarely exceed 200,000 calories per gram-atom, energies of 10 to 20 billion calories per gram-atom are not uncommon in transmutations. These tremendous energies result from the conversion of matter to energy in accordance with the Einstein equation $E = mc^2$, referred to in 7.2.

1. By alpha particle (helium ion) bombardment

(1)	${}_{13}Al^{27} + {}_{2}He^{4} = {}_{15}P^{30} + {}_{0}n^{1}$	${}^{27}_{13}Al(\alpha,n){}^{30}_{15}P$
(2)	${}_{96}Cm^{242} + {}_{2}He^{4} = {}_{98}Cf^{244} + 2\,{}_{0}n^{1}$	${}^{242}_{96}Cm(\alpha,2n){}^{244}_{98}Cf$
(3)	${}_{7}N^{14} + {}_{2}He^{4} = {}_{8}O^{17} + {}_{1}H^{1}$	${}^{14}_{7}N(\alpha,p){}^{17}_{8}O$

2. By neutron bombardment

(4)	${}_{7}N^{14} + {}_{0}n^{1} = {}_{6}C^{14} + {}_{1}H^{1}$	${}^{14}_{7}N(n,p){}^{14}_{6}C$
(5)	${}^{19}_{9}F + {}^{1}_{0}n = {}^{16}_{7}N + {}^{4}_{2}He$	${}^{19}_{9}F(n,\alpha){}^{16}_{7}N$
(6)	${}_{7}N^{14} + {}_{0}n^{1} = {}_{7}N^{13} + 2\,{}_{0}n^{1}$	${}^{14}_{7}N(n,2n){}^{13}_{7}N$
(7)	${}_{92}U^{238} + {}_{0}n^{1} = {}_{92}U^{239} + \gamma$	${}^{238}_{92}U(n,\gamma){}^{239}_{92}U$

3. By proton bombardment

(8)	${}_{5}B^{11} + {}_{1}H^{1} = {}_{6}C^{11} + {}_{0}n^{1}$	${}^{11}_{5}B(p,n){}^{11}_{6}C$
(9)	${}^{14}_{7}N + {}^{1}_{1}H = {}^{11}_{6}C + {}^{4}_{2}He$	${}^{14}_{7}N(p,\alpha){}^{11}_{6}C$
(10)	${}^{9}_{4}Be + {}^{1}_{1}H = {}^{8}_{4}Be + {}^{2}_{1}D$	${}^{9}_{4}Be(p,d){}^{8}_{4}Be$
(11)	${}_{7}N^{14} + {}_{1}H^{1} = {}_{8}O^{15} + \gamma$	${}^{14}_{7}N(p,\gamma){}^{15}_{8}O$

4. By deuteron bombardment

(12)	${}_{11}Na^{23} + {}_{1}D^{2} = {}_{11}Na^{24} + {}_{1}H^{1}$	${}^{23}_{11}Na(d,p){}^{24}_{11}Na$
(13)	${}_{6}C^{12} + {}_{1}D^{2} = {}_{7}N^{13} + {}_{0}n^{1}$	${}^{12}_{6}C(d,n){}^{13}_{7}N$
(14)	${}^{16}_{8}O + {}^{2}_{1}D = {}^{14}_{7}N + {}^{4}_{2}He$	${}^{16}_{8}O(d,\alpha){}^{14}_{7}N$
(15)	${}^{37}_{17}Cl + {}^{2}_{1}D = {}^{37}_{18}A + 2\,{}^{1}_{0}n$	${}^{37}_{17}Cl(d,2n){}^{37}_{18}A$

5. By gamma ray bombardment

(16)	${}^{9}_{4}Be + \gamma = {}^{8}_{4}Be + {}^{1}_{0}n$	${}^{9}_{4}Be(\gamma,n){}^{8}_{4}Be$

8.11 Artificial radioactivity. Of the hundreds of nuclides that have been prepared to date by transmutation as discussed in Sections 8.8, 8.9, and 8.10, more than 500 are unstable and undergo spontaneous radioactive decay. These artificially prepared radioactive nuclides

are called *radioelements*. The following sets of equations illustrate the preparation and decay of some typical radioelements.

(1) $${}_5B^{10} + {}_2He^4 = {}_7N^{13} + {}_0n^1$$

$${}_7N^{13} \xrightarrow[9.9\ m]{+1e^0} {}_6C^{13}$$

The ejected particle is a *positron* ($_{+1}e^0$); it has the same mass as an electron, but its charge is $+1$, whereas the charge of an electron is -1. A positron is formed from a proton by the reaction

$$\text{proton} - \text{positron} = \text{neutron}$$

The loss of a positron will therefore decrease the atomic number (charge on the nucleus) by 1.

(2) $${}^{31}_{15}P + {}^{2}_{1}D = {}^{32}_{15}P + {}^{1}_{1}H$$

$${}^{32}_{15}P \xrightarrow[14.3\ d]{-1e^0} {}^{32}_{16}S$$

(3) $${}^{59}_{27}Co + {}^{1}_{0}n = {}^{60}_{27}Co + \gamma$$

$${}^{60}_{27}Co \xrightarrow[5.3\ y]{-1e^0,\gamma} {}^{60}_{28}Ni$$

(4) $${}_{12}Al^{27} + {}_2He^4 = {}_{15}P^{30} + {}_0n^1$$

$${}_{15}P^{30} \xrightarrow[3\ m]{+1e^0} {}_{14}Si^{30}$$

(5) $${}_{11}Na^{23} + {}_0n^1 = {}_{11}Na^{24} + \gamma$$

$${}_{11}Na^{24} \xrightarrow[14.8\ h]{-1e^0} {}_{12}Mg^{24}$$

8.12 The neutrino. Evidence indicates that there is produced in the decay of some radioactive nuclides a particle of very small mass (comparable with that of a beta particle) and zero charge. This particle is called the *neutrino*. Although little is known about the neutrino, its existence is of importance because it accounts for certain mass and energy changes in many radioactive disintegrations.

8.13 Some practical uses of radioelements. 1. *Use of specific nuclides as tracer elements in scientific research.* The use depends upon the following facts.

(a) A radioactive isotope has the same chemical properties as the stable modification, and will therefore form the same compounds and take part in the same reactions. A compound containing the radioactive isotope of an element will react exactly the same as the same compound containing a stable isotope.

(b) The presence of a radioactive isotope, and its concentration, can be determined by the use of a Geiger-Mueller counter.

The following example will illustrate this use. When BaO is heated to 500°C the following reaction takes place:

(1) $$2\,BaO + O_2 = 2\,BaO_2$$

When the BaO_2 is heated to 1000°C it decomposes according to the reaction

(2) $$2\,BaO_2 = 2\,BaO + O_2$$

We would like to know whether or not any of the oxygen that is present in the BaO with which we start in reaction (1) is given off as oxygen gas in reaction (2). To answer this question we will first prepare some radioactive BaO by burning stable barium in an atmosphere of a radioactive oxygen isotope. The resulting BaO is said to contain a *tagged* oxygen atom and is normally represented by the formula BaO*. The O* means that the O is radioactive. The radioactive oxygen atom is said to be *"tagged"* because it can easily be detected or located because of its radioactivity. Having prepared the BaO* we will measure its activity (the quantity of its radioactive emanations); this activity gives us a direct measure of its O* content.

We will now heat the BaO* to 500°C in an atmosphere of ordinary stable oxygen gas. The following reaction will then take place. (For convenience in differentiating the oxygen atoms, the formula of barium peroxide will be represented as BaO.O rather than BaO_2.)

(3) $$2\,BaO^* + O_2 = 2\,BaO^*.O$$

We will next heat the BaO*.O prepared in equation (3) to 1000°C, collect all the oxygen gas evolved, and test it for radioactivity. If it shows *no radioactivity* we can conclude that none of the oxygen present in the original BaO is evolved as oxygen gas when the peroxide is heated. The equation for the decomposition of the BaO*.O will then be

(4) $$2\,BaO^*.O = 2\,BaO^* + O_2$$

If the oxygen gas that is given off is radioactive this activity must be due to O* atoms that were originally present in the BaO*. That means that some of the oxygen present as BaO is given off as O_2 gas when the BaO_2 which is prepared from this BaO at 500°C is heated to 1000°C.

By comparing the activity of the BaO* formed as a product in equation (4) with the activity of the BaO* used in equation (3), we can

determine the extent to which the oxygen atoms have exchanged places in the course of the reaction.

Hundreds of similar examples could be cited. The use of tagged atoms to follow the course of a reaction or trace the path of an element in a biological or industrial process has proved to be an invaluable research tool.

2. *Use of radioactive isotopes for treatment of specific diseases or specific types of infection.* The use of radioactive iodine for treatment of hyperthyroidism (goiter) is a good example. Iodine, taken into the body as sodium iodide or other iodine compound, collects in the thyroid gland. This is true whether the iodine is stable or radioactive. Infection of the thyroid gland can be treated by giving the patient the correct amount of radioactive iodine of the proper activity. This tagged iodine will collect in the thyroid gland; the radioactive rays which it emits will reduce or eliminate the hyperthyroidism.

Additional examples are: use of tagged phosphorus for treatment of certain diseases of the blood stream, radioactive gold and strontium for treatment of cancer, and Co^{60} as a substitute for radium and radon in the treatment of cancer. Radioactive cobalt-60 of almost any desired activity can be prepared by bombardment of ordinary cobalt metal with neutrons in the nuclear reactor. This cobalt decays with the emission of beta and gamma rays of high intensity. Consequently, it is an effective substitute for radium and radon in the treatment of malignant tumors. It costs about one one-hundredth as much as an equivalent amount of radium and is much more convenient to use.

8.14 Nuclear fission. When the nuclei of certain heavy atoms are bombarded by neutrons an unusual type of transmutation takes place; the atoms actually burst into two fragments. This bursting of an atom as a result of neutron bombardment is called *nuclear fission.*

The only elements which are known to undergo fission *readily* are U^{235}, U^{233}, and Pu^{239}. The isotope U^{235} is a component of natural uranium in which it occurs mixed with U^{238} to the extent of about 0.7%. The isotope U^{233} does not occur in nature but can be prepared from natural Th^{232} by the reactions

$$_{90}Th^{232} + {}_{0}n^{1} = {}_{90}Th^{233} + \gamma$$

$$_{90}Th^{233} \xrightarrow[23.5\ m]{\beta} {}_{91}Pa^{233}$$

$$_{91}Pa^{233} \xrightarrow[27.4\ d]{\beta} {}_{92}U^{233}$$

Element Pu^{239} does not occur in nature, but can be prepared from U^{238}

by the reactions

$$_{92}U^{238} + {}_{0}n^{1} = {}_{92}U^{239} + \gamma$$

$$_{92}U^{239} \xrightarrow[23.5\ m]{\beta} {}_{93}Np^{239}$$

$$_{93}Np^{239} \xrightarrow[2.3\ d]{\beta} {}_{94}Pu^{239}$$

8.15 Changes accompanying the fission process. When a quantity of fissionable substance ($_{92}U^{235}$ for example) fissions, the following changes take place.

1. Each fission fragment, being made up of protons and neutrons, rearranges itself to form the nucleus of a new lighter element, and by gathering up the required number of electrons from the surrounding atmosphere, becomes an atom of a new element. Different atoms of U^{235} do not necessarily burst at the same point; therefore the fissioning of a quantity of the nuclide yields a mixture of elements. A sum total of about 40 different elements have been identified among the products of all U^{235} fissions carried out to date. The fragments formed when the atom bursts fly apart at terrific velocities.

2. A large amount of heat energy is evolved. The actual value is close to 24 billion calories for each gram of U^{235} fissioned. This is about 3 million times as much heat as is given off when a gram of ordinary coal burns. The excessive amount of heat results from the fact that matter disappears and heat energy is created in its place in the ratio of about 21 trillion calories per gram of matter. When U^{235} fissions, about 0.1% of the mass of the uranium disappears as matter and appears as kinetic energy and gamma radiation (88% as energy and 12% as radiation). The conversion of matter into energy is in accord with *Einstein's* equation $E = mc^2$, referred to in 7.2.

3. A large amount of high-energy gamma radiation is given off. This radiation is very penetrating and extremely destructive.

4. A large number of high-energy neutrons are ejected. When an atom of U^{235}, in which the neutron-proton ratio is 143 to 92, fissions to form atoms of $_{54}Xe^{138}$ and $_{39}Y^{95}$, for example, the neutron-proton ratio drops to 140 to 93. This means that about 3 free neutrons are formed when each atom fissions. These 3 neutrons can then fission 3 atoms of U^{235}; this will liberate 9 neutrons, and they in turn will fission 9 atoms of U^{235}. This cycle will continue, with the number of atoms fissioned being tripled each time. As a result the over-all reaction will go faster and faster until finally, if sufficient U^{235} is present, it will go so fast that a tremendous explosion will result. This is exactly what happens in an atom bomb. A reaction, such as the one pictured above, which speeds

up because the reaction yields increasing amounts of reactant is called a *chain reaction* (see Figure 8.10). In actual practice only about 2 of the 3 extra neutrons that are liberated in each fission process produce additional fissioning. That still gives a chain reaction, one that is so extremely rapid that, for all practical purposes, it produces an almost instantaneous explosion when a mass of U^{235} or Pu^{239} is bombarded with neutrons.

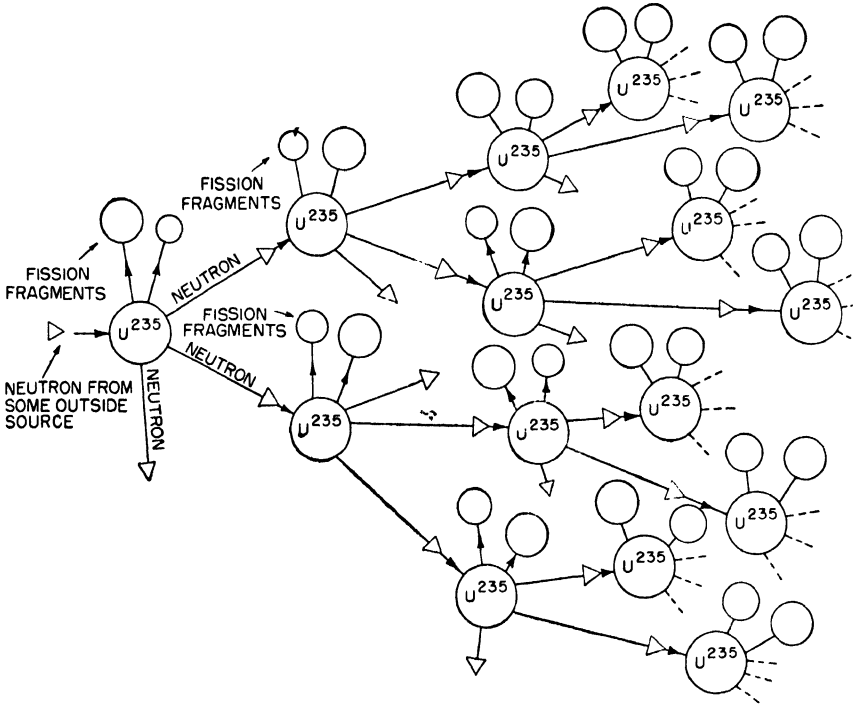


Figure 8.10. A nuclear chain reaction: the fissioning of U^{235} by neutrons.

8.16 Uses of nuclear fission. Some of the actual and possible uses of nuclear fission are:

1. Production of superbombs. This use has been perfected to the point where "A" bombs of terrible destructiveness are available as combat weapons.

2. As a source of power for industry, for heating, and for propelling ocean-going vessels and aircraft. This use depends upon the immense quantity of heat energy that is given off in the fission process. The potentialities of nuclear fission for this use have not yet been fully developed but its inherent problems are rapidly being solved. It is entirely

possible that nuclear fission may some day be the world's major source of power.

3. Production of radioelements for use in medicine, in industry, and in research. Already large quantities of a great many different radioelements have been produced for this purpose in nuclear reactors (see Figure 8.11). These reactors, or "piles" as they are commonly called, are essentially furnaces in which a combined transmutation and fission process is going on at a controlled rate. Elements to be transmuted are placed in the reactor for definite lengths of time. Bombardment by the

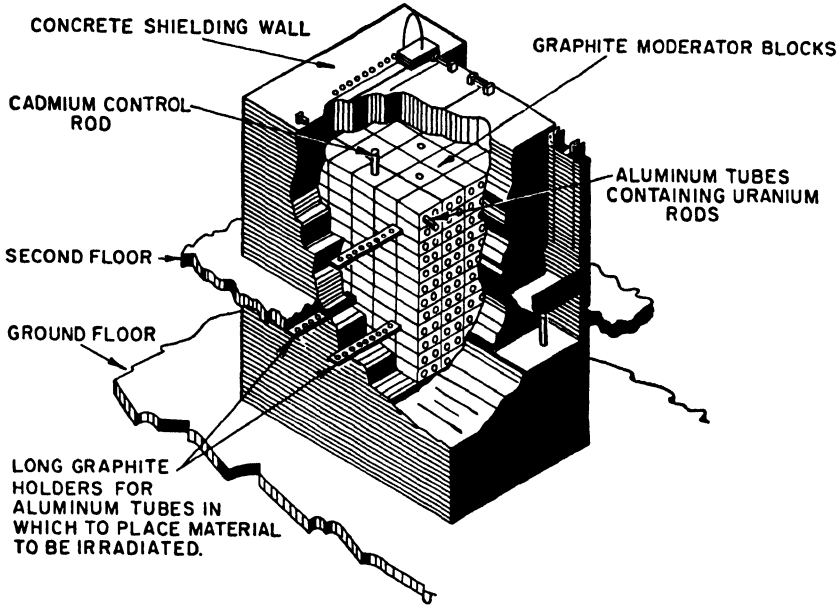


Figure 8.11. General plan of a nuclear reactor using graphite as a moderator.

neutrons and gamma rays generated in the fission process produces the desired transmutation and gives a useful radioelement. Thus bombardment of Co^{59} produces radioactive Co^{60}. The U^{235} or Pu^{239} which serves as the fuel in the reactor is suspended in or surrounded by layers of graphite or heavy water (D_2O); these materials slow down the neutrons which are emitted by the "fuel" so that they can be "captured" by the material being bombarded. A material which slows down the speed of neutrons is called a *moderator*.

8.17 Nuclear fusion. The principal source of the sun's energy is postulated to be the net over-all reaction

$$4\,H = He + \text{energy}$$

The process represented by this reaction is called *nuclear fusion;* four light nuclei have been "fused" together to form a heavier nucleus. The fusion process is accompanied by a loss of matter, in accordance with the Einstein equation $E = mc^2$, and this matter is converted into heat energy in the ratio of about 21 trillion calories for each gram of matter lost.

It has been determined by experiment that, with the energy liberated by an "A" bomb explosion or an analogous fission process as a source of heat with which to trigger (initiate) the reaction, it is possible to carry out a fusion of deuterium (H^2) and tritium (H^3) in accordance with the reaction

$$_1H^2 + {}_1H^3 = {}_2He^4 + {}_0n^1 + \text{energy}$$

Lithium and hydrogen can be fused in a similar manner to yield helium. The stupendous amount of heat generated when a sizable quantity of Li^7 and H^2 or H^2 and H^3 are fused creates a tremendous explosion. The hydrogen bombs (thermonuclear bombs) that have been exploded probably contained lithium and hydrogen or other low-mass fusionable elements, and probably were triggered by a fission reaction.

8.18 Transmutation and atomic structure. It should be emphasized that all the experimental facts that have been noted in connection with transmutation, artificial radioactivity, nuclear fission, and nuclear fusion support the concept that the nucleus of the atom is made up of neutrons and protons; they add reality to the *theory* of the structure of the atom.

8.19 Cosmic rays. Mesons. A mixture of rays of very high energy and penetrating power is continually coming to us from somewhere in or beyond the earth's atmosphere. They consist largely of electrons, positrons, *mesons*, and *photons* (light) which are believed to have been formed as the result of the impact of high-speed protons and atomic nuclei on nuclides found in the outer reaches of our atmosphere. These high-speed protons and nuclei and the mixture of rays which they generate are called *cosmic rays.* They are believed to have originated from reactions that are taking place in other parts of the cosmos. They are estimated to have about a billion times as much energy as that of the most energetic particle that can be produced in a giant cyclotron. Some of the primary cosmic rays penetrate the atmosphere and reach the earth's surface; most of them are probably destroyed by impact

with atmospheric nuclides, and their effect is transmitted to us in the form of positrons and mesons.

Two kinds of *mesons* have been identified, *pi-mesons* and *mu-mesons*. The masses of pi-mesons and mu-mesons are, respectively, 275 and 210 times as great as that of an electron. Pi-mesons and mu-mesons can both be either positively or negatively charged; pi-mesons can also be neutral, the mass of this neutral modification being about 263 times as great as that of an electron.

Cosmic rays are of great scientific interest because they indicate that reactions analogous to those that occur in nuclear fusion and nuclear fission are probably taking place in other parts of the cosmos.

Questions and Problems

1. Define or describe and illustrate each of the following: radioactivity; alpha ray; beta ray; gamma ray; half-life; disintegration series; transmutation; radioelement; tagged atom; nuclear fission; nuclear fusion; nuclear reactor; positron; neutrino; meson; cosmic rays; chain reaction; thermonuclear reaction.

2. Describe the available methods that can be used to determine whether or not a substance is radioactive.

3. Describe how the concentration of the radioactive component of a mixture can be determined.

4. How can the approximate age of the earth be calculated from the composition of a sample of uranium ore?

5. List the important uses of natural radioactive materials and point out the basis for each use.

6. Why must radioactive material that is being handled by an individual be heavily shielded with lead?

7. How do alpha, beta, and gamma rays compare in mass, charge, speed, and penetrating power?

8. List the projectiles that are used for bombardment in transmutation and give a common source of each.

9. Point out, briefly, how each of the following operates to produce a high-speed nuclear projectile: cyclotron; van de Graaff generator; linear accelerator.

10. Describe the important uses of radioelements.

11. Describe how you could determine, by the use of radioactive tracer elements, whether, in the reaction $KClO_3 + 6\,HCl = KCl +$

$3\ Cl_2 + 3\ H_2O$, any of the evolved chlorine gas was originally present in the $KClO_3$.

12. Describe how, by the use of radioactive tracers, you could:

(a) Determine whether a long strip of metal was of uniform thickness.

(b) Determine whether iron in the form, $Fe_2(SO_4)_3$, is assimilated by the body and appears as the iron component of hemoglobin.

(c) Measure the rate at which iodine, which is taken into the stomach, is absorbed by the thyroid gland.

13. Give the transmutation reaction by which a new element which does not occur in nature has been synthesized.

14. List the changes that occur during nuclear fission.

15. List the possible uses to which nuclear fission may be put.

16. Point out how a nuclear fission is initiated and describe the chain reaction by which it is accelerated.

17. Point out the principle upon which the hydrogen bomb is believed to operate.

18. Account for the tremendous evolution of heat energy during nuclear fission and nuclear fusion.

19. Account for the neutrons which are evolved when a heavy nucleus is fissioned.

20. Point out just how the experimental facts relating to natural radioactivity, transmutation of elements, artificial radioactivity, nuclear fission, and nuclear fusion support the modern theory of the structure of the atom.

21. Complete the following equations, designating in each the symbol, mass, and charge of the missing unit.

(a) ${}_{92}U^{235} = {}_{90}Th^{231} + \ldots\ldots\ldots\ldots$

(b) ${}_{91}Pa^{231} = \ldots\ldots\ldots\ldots + {}_{2}He^{4}$.

(c) $\ldots\ldots\ldots\ldots = {}_{83}Bi^{211} + {}_{-1}e^{0}$.

(d) ${}_{7}N^{13} = {}_{6}C^{13} + \ldots\ldots\ldots\ldots$

(e) ${}_{95}Am^{241} + {}_{2}He^{4} = {}_{97}Bk^{243} + \ldots\ldots\ldots\ldots$

(f) ${}_{4}Be^{9} + \ldots\ldots\ldots\ldots = {}_{6}C^{12} + {}_{0}n^{1}$.

(g) ${}_{13}Al^{27} + {}_{2}He^{4} = {}_{14}Si^{30} + \ldots\ldots\ldots\ldots$

(h) ${}_{8}O^{18} + \ldots\ldots\ldots\ldots = {}_{9}F^{18} + {}_{0}n^{1}$.

(i) ${}_4Be^9 + {}_1H^1 = {}_4Be^8 + \ldots\ldots\ldots\ldots$

(j) ${}_6C^{12} + {}_1H^1 = {}_7N^{14} + \ldots\ldots\ldots\ldots$

(k) ${}_{17}Cl^{37} + {}_1D^2 = \ldots\ldots\ldots\ldots + {}_1H^1$.

(l) ${}^{85}_{37}Rb + {}_0n^1 = {}^{85}_{36}Kr + \ldots\ldots\ldots\ldots$

(m) ${}^{14}_7N(n,2n) \ldots\ldots\ldots\ldots$

(n) ${}^{11}_5B(p,\ldots\ldots\ldots){}^{11}_6C$.

(o) ${}^{16}_8O(\ldots\ldots\ldots,\alpha){}^{14}_7N$.

(p) $\ldots\ldots\ldots(n,\gamma){}^{80}_{35}Br$.

22. The sodium isotope of mass number 24 is radioactive, a beta particle being emitted during its disintegration. Of what element is the product element an isotope and in what group and period of the periodic table does it fall?

23. When the isotope of boron with mass number of 10 is bombarded with alpha particles an isotope of nitrogen is produced as a product. List each known particle that might possibly have been ejected, keeping in mind that only one kind of particle is emitted in a specific transmutation.

24. When the aluminum nuclide with a mass number of 27 captures a neutron a proton is ejected. How many p orbital electrons does the new element which is formed contain?

CHAPTER 9

Water

9.1 The importance of water. Water is the most abundant, the most widely distributed, and the most commonly used of all chemical compounds. In the oceans, lakes, and rivers it covers nearly three-fourths of the surface of the earth. It constitutes about 70% of the weight of the human body and represents as much as 95% of the weight of some plants and fruits. It is the liquid medium in blood and all other animal and vegetable fluids. Its evaporation from the surface of the skin in the form of perspiration helps maintain normal body temperature, and its high capacity for absorbing heat is a prime factor in controlling the temperatures of various parts of the earth's surface. It provides waterways for the thousands of boats and barges that transport the world's goods and is our most important means of intercontinental communication. Energy derived from falling water provides the world with a major part of its light and power. Through the medium of bathing, swimming, fishing, boating, canoeing, sailing, and other water sports it provides recreation for millions of people. Abundance or scarcity of water, in the form of rain, spells crop abundance or crop scarcity and means, every year, the difference between life and death to thousands of people.

9.2 Physical properties of water. 1. *It is a tasteless, odorless liquid.* Thin layers are colorless but in thicker layers it has a greenish-blue color.

2. *It freezes at* 0°C (32°F). As has already been noted, the freezing point of water represents a fixed point on both the centigrade and Fahrenheit temperature scales.

3. *It boils at* 100°C (212°F) *at a pressure of* 760 mm. The boiling point of water is a second fixed point on the centigrade and Fahrenheit scales. The decrease in boiling point of a liquid with decrease in pressure has already been noted; that is why water will boil at about 85°C on Pikes Peak and at 250°F in a pressure cooker.

4. *Its heat of fusion (as ice) is* 79.7 cal/g.

5. *Its heat of vaporization is* 539.6 cal/g. This accounts for the large cooling effect which results when water evaporates. It is the basis for

the effectiveness of steam as a heating agent in home and industrial heating systems and accounts for the severity of steam burns; each gram of steam which condenses gives up 539.6 calories of heat.

6. *It has a density of* 1 g/cc *at* 4°C. The cubic centimeter was originally defined as the volume occupied by 1 gram of water at 4°C. A liter is, by present definition, the volume occupied by 1 kilogram of water at 4°C. As has already been noted, a kilogram of water occupies a volume of exactly 1000.027 cubic centimeters. One milliliter is therefore equal to 1.000027 cc, and the exact density of water at 4°C is 1 g/ml or 1 g/1.000027 cc. For all practical purposes, however, the density of water at 4°C is 1 g/cc.

The densities of all liquids increase when the temperature is lowered; that is equivalent to saying that the volume of a mass of the liquid decreases as the temperature decreases. Water, however, is unique in its behavior. Its density increases (volume shrinks) regularly on cooling from 100°C (its boiling point) to 4°C, but from 4°C to 0°C it reverses itself and the density *decreases* (volume increases). That means that its *maximum density* is at 4°C. This is illustrated in Table 9.1. It should be noted in this table that, while the density of water at 0°C is 0.9998, the density of ice at 0°C is 0.9170. That explains why ice floats in water and why about one-eleventh of the volume of a floating iceberg sticks out of the water. It also accounts for the fact that the freezing of water will burst water pipes, disintegrate rocks, pulverize soil, and crack the block of a water-cooled automobile engine.

TABLE 9.1

DENSITY OF WATER AND ICE

Temperature (°C)	*Density* (g/cc)	*Temperature* (°C)	*Density* (g/cc)
100	0.9586	10	0.9997
80	0.9719	5	0.9999
60	0.9833	4	1.0000
40	0.9923	0	0.9998
20	0.9982	0 (ice)	0.9170

The changes in density noted in Table 9.1 are of vital importance to the existence of marine life in lakes located in climates where the water temperatures fall below 0°C. As the surface water cools, by contact with cold air and to a lesser extent by evaporation, its density increases. This causes it to sink, and warmer water rises to take its place. This process, referred to as "turnover," goes on during the three or four fall months. By the time the lake begins to freeze most of its water has taken one or more trips to the surface. While at the surface it dissolves

some air, and then, on cooling, carries this air back with it into the depths of the lake. This air is necessary if fish are to live in the water.

If ice were heavier than water, even the deepest lakes would, in cold climates, freeze solid to the bottom. This, obviously, would destroy marine life.

7. *It has a specific heat (heat capacity) of* 1 cal/g/deg. Water has the highest specific heat of the common liquids. It is used as a standard in defining the calorie and in measuring specific heat; a calorie is the quantity of heat required to raise the temperature of 1 g of water 1 deg centigrade. Since the specific heat of a substance is the quantity of heat in calories required to raise the temperature of 1 g of the substance 1 deg centigrade, it follows that the specific heat of water is 1 cal/g/deg. Because of its high specific heat, water is widely used as a cooling agent in the cooling systems of engines and as a carrier of heat in hot-water house-heating systems and hot-water bottles. It is this high heat capacity which modifies the temperature of a region near a large body of water and keeps it from changing suddenly and widely.

8. *It is a covalent compound.* This is shown, experimentally, by the fact that it is a very poor conductor of electricity and that ice does not have an ionic crystal lattice. The two hydrogen atoms are attached to the oxygen atom by simple covalent bonding in the manner illustrated in Figure 9.1.

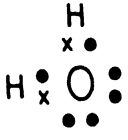


Figure 9.1. The H_2O molecule.

9. *It is a strongly polar compound.* Because of the strongly electronegative character of the oxygen atom, its nucleus exerts such a strong attractive pull on the hydrogen electrons that they are drawn out of their normal position in relation to the hydrogen nucleus. Also, the 2 hydrogen atoms are bonded to the oxygen atom at an angle of 105° rather than being set in a straight line (see Figure 9.1). As a result of these two factors, a dipole is formed in which the hydrogen end has a positive polarity, while the oxygen end is negative, as illustrated in Figure 9.2. Because the hydrogen electrons are drawn so far out of their normal position, the hydrogen nucleus behaves somewhat like a proton; it may share 2 electrons with the oxygen atom of an adjacent H_2O molecule, forming what is referred to as a *hydrogen bond.*

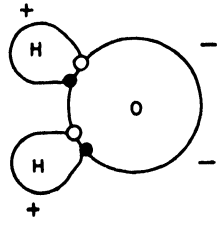


Figure 9.2. Polarity of the H_2O molecule.

By comparison with the other binary hydrogen compounds of group VIA (H_2S, H_2Se, and H_2Te), water has an abnormally high freezing

point and boiling point (see Table 9.2). Had H_2O followed the pattern set by H_2Te, H_2Se, and H_2S, in which the melting points and boiling points decrease as the molecular weights of the compounds decrease, the melting point of ice would have been near $-95°C$ and the boiling point of water near $-65°C$.

TABLE 9.2

FREEZING POINTS AND BOILING POINTS OF THE GROUP VIA BINARY HYDROGEN COMPOUNDS

Compound	*Mol Wt*	*Melting Point* (°C)	*Boiling Point* (°C)
H_2O	18	0	100
H_2S	34	−85.5	−60.3
H_2Se	81	−64.0	−41.3
H_2Te	129.6	−49.0	−2.2

The out-of-line high values for H_2O can be accounted for by the combined effect of hydrogen bonding and the high polarity of its molecules. Both factors cause formation of large "clusters" of H_2O molecules, giving the effect of high molecular weight, and consequently, high melting and boiling points. Because S, Se, and Te are less negative than O, the H_2S, H_2Se, and H_2Te molecules are not strongly polar and there is no hydrogen bonding. Therefore these compounds have normally low melting points and boiling points.

The fact that HF, which is derived from the strongly electronegative element F, and hence is strongly polar and displays strong hydrogen bonding, also has an abnormally high melting and boiling point and is out of line with respect to HCl, HBr, and HI in the same way that H_2O is out of line with H_2S, H_2Se, and H_2Te, lends support to the view that the abnormality of H_2O and HF is attributable to their strongly hydrogen-bonded and polar character.

10. *It is an excellent solvent.* The character of water as a solvent will be discussed in detail in Chapter 11. We can anticipate the discussion by stating that it will dissolve a great many electrovalent compounds and polar covalent compounds and that its outstanding solvent action toward these compounds is probably due to its own strongly dipolar character. The water dipoles exert an electrostatic as well as a gravitational pull on the ions of the electrovalent compounds and the dipoles of the polar covalent compounds.

9.3 The chemical properties of water

1. *Cold water + metal more reactive than* Mg = *hydrogen + hydroxide of the metal*

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

This reaction has already been given as a laboratory source of hydrogen. It illustrates the fact that metals are base-forming elements. It should be noted that all metals of group IA, and all those of group IIA except Mg and Be, will react with cold water. In both groups the reactivity of the metal toward cold water decreases as the atomic number decreases. The group IA and IIA metals are the most reactive and most strongly electropositive. The more strongly electropositive the metal, the more rapidly it liberates hydrogen from cold water. The group IA and IIA metals have oxidation numbers (valences) of +1 and +2, respectively.

In each of the above reactions the metal is the reducing agent, and water is the oxidizing agent. The metal is oxidized, since its oxidation number increases from 0 in the free metal to +1 (or +2) in the hydroxide. Hydrogen is reduced, since its oxidation number decreases from +1 in H_2O to 0 in H_2. The greater the electropositivity of the metal the greater its strength as a reducing agent.

2. *Hot water or steam + metal less reactive than* Ca *but more reactive than* H = *hydrogen + oxide of the metal*

$$H_2O\ (\text{heated}) + Mg = MgO + H_2$$
$$H_2O\ (\text{heated}) + Zn = ZnO + H_2$$

The less reactive the metal, the higher the temperature required to cause a reaction to take place. Metals below hydrogen in the activity series (Table 3.3, page 80) will not react with steam.

In each reaction the metal is the reducing agent, while H_2O is the oxidizing agent. The metal is oxidized, while hydrogen is reduced.

The hydroxides of the metals decompose to give the metal oxide and water when heated to high temperatures; that is why the oxide rather than the hydroxide is formed in the reactions shown above.

3. *Water + oxide of a metal = hydroxide of the metal*

$$H_2O + Na_2O = 2\,NaOH$$
$$H_2O + CaO = Ca(OH)_2$$

These reactions indicate that the oxides of metals are basic in character and that metals are base-forming elements.

The oxides of the metals more reactive than Mg (the metals that react with cold water) are very soluble in water. The oxides of all other metals are sparingly soluble; they react only slightly with water to form the hydroxide.

4. *Water + oxide of a nonmetal = a ternary acid*

$$H_2O + SO_2 = H_2SO_3 \text{ (sulfurous acid)}$$
$$H_2O + CO_2 = H_2CO_3 \text{ (carbonic acid)}$$
$$6\,H_2O + P_4O_{10} = 4\,H_3PO_4 \text{ (phosphoric acid)}$$
$$H_2O + N_2O_5 = 2\,HNO_3 \text{ (nitric acid)}$$

These reactions illustrate the fact that nonmetals are acid-forming elements, and that the oxides of nonmetals are acidic in character. Not all nonmetal oxides are equally soluble in water; some are insoluble.

As has been noted in Chapters 6 and 7, the nonmetals fall in the right-hand section of the periodic table above and to the right of the zigzag diagonal line running below B, Si, As, Te, and At. In each of groups IIIA, IVA, VA, VIA, and VIIA, as the atomic number increases, the nonmetallic character and electronegativity of the element decreases. In line with this decrease in nonmetallic character, the solubility in water of the oxide decreases as the atomic number increases. To illustrate, in group IIIA, boric oxide, B_2O_3, is moderately soluble in water and forms the weak acid, H_3BO_3.

$$B_2O_3 + 3\,H_2O = 2\,H_3BO_3$$

The oxides of aluminum, gallium, indium, and thallium are insoluble in water, and become increasingly more basic in character in the order listed.

In group IVA, CO_2 is moderately soluble, while SiO_2 and the oxides of germanium, tin, and lead are insoluble and are increasingly basic in character. Likewise, in group VA, N_2O_3, N_2O_5, P_2O_3, and P_2O_5 are highly soluble, As_2O_3 and As_2O_5 are sparingly soluble, while Sb_2O_5 and Bi_2O_3 are insoluble. The group VIA and VIIA elements are all distinctly nonmetallic in character and their oxides are all either moderately or highly soluble in water, the solubility decreasing as the atomic number increases.

5. *Water + sodium peroxide = oxygen + sodium hydroxide*

$$2\,H_2O + 2\,Na_2O_2 = O_2 + 4\,NaOH$$

This is a laboratory method for preparing oxygen.

6. *Water + hydride of a metal = hydrogen + metal hydroxide*

$$H_2O + KH = H_2 + KOH$$
$$2\,H_2O + CaH_2 = 2\,H_2 + Ca(OH)_2$$

Since only the more reactive metals (those more electropositive than magnesium) form stable hydrides, the hydroxide will be soluble and the

resulting solution will show a basic test toward litmus. This reaction is used to some extent by the armed forces and the weather bureau for small-scale on-the-spot preparation of hydrogen gas for inflating observation balloons. All that is needed is a simple generator which will allow cold water to be added, dropwise, to solid CaH_2. The CaH_2 is easily transported and stored, and water is generally readily available. One mole (42 g or about 1.5 oz) of CaH_2 will yield 2 moles (44.8 l at STP) of hydrogen gas. The CaH_2 is also used as a reducing medium in reactions that must be carried out in basic solution.

The hydrides are electrovalent compounds. The active metal transfers its valence electron (or electrons) and thereby becomes a positive ion. Each atom of hydrogen receives an electron, thereby becoming a negative ion with the inert helium gas structure. The resulting electrovalent character of the hydride can be designated by the formulas K^+, H^- and Ca^{++}, H_2^{--}; the hydrogen has an oxidation number of -1. It follows, therefore, that in the above reactions hydrogen is both oxidized and reduced; the hydrogen in the hydride is oxidized from an oxidation number of -1 to 0 (in H_2), while one atom of hydrogen in H_2O is reduced from an oxidation number of $+1$ (in H_2O) to 0 (in H_2). The hydride is the reducing agent, while H_2O is the oxidizing agent.

7. *Electrolysis of water yields hydrogen and oxygen.*

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

This is a commercial method for preparing hydrogen and oxygen. Sulfuric acid is added to the water to produce a conducting solution.

8. *Water can be thermally decomposed.* If water (steam) is heated in a closed container to a temperature of 1900°C or higher, some decomposition into H_2 and O_2 takes place. Since, as we have learned in Chapter 4, hydrogen, when heated, combines with oxygen to form H_2O, the H_2 and O_2 which are formed in the thermal decomposition recombine to form H_2O. An *equilibrium* is thus set up as represented by the equation

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

At equilibrium the *rate* at which H_2O is decomposing is exactly the same as the *rate* at which H_2 and O_2 are combining to form H_2O. At 1900°C about 1% of the original water is decomposed, while at 2500° the per cent is about 7.

9. *Oxidation of carbon by steam*

$$H_2O\ (\text{steam}) + C\ (\text{heated}) = CO + H_2$$

The mixture of CO and H_2 is known as *water gas* and is used as a commercial fuel gas.

In the presence of a catalyst and excess steam the products are CO_2 and H_2.

$$C + 2\,H_2O\ (\text{heat, catalyst}) = CO_2 + 2\,H_2$$

This has already been referred to as a commercial method for preparing hydrogen.

10. *Water + certain anhydrous salts = hydrates*

If cold water is added to cold, white, anhydrous (waterfree) copper sulfate, $CuSO_4$, the white solid turns blue and heat is given off. If the product is dissolved in water and the resulting solution is evaporated to a small volume and then allowed to cool, a blue crystalline solid will separate out. This blue solid can be shown by analysis to contain $CuSO_4$ and H_2O combined in the exact ratio of 1 mole of $CuSO_4$ to 5 moles of H_2O. It is therefore a definite chemical compound and has the formula $CuSO_4 \cdot 5H_2O$. The solid can be wiped completely dry; there is no visible sign of water. However, if it is heated it will yield pure water and pure $CuSO_4$ in the exact ratio represented by the formula $CuSO_4 \cdot 5H_2O$. This suggests that the water is present in the blue crystalline solid as H_2O molecules. The equation for the reaction is

$$CuSO_4 + 5\,H_2O = CuSO_4 \cdot 5H_2O$$

The product is called *hydrated* copper sulfate, and the 5 molecules of water are referred to as *water of hydration* or *water of crystallization.*

A great many hydrated salts are known; each contains its own specific number of molecules of water of hydration. Thus we find $Na_2CO_3 \cdot 10H_2O$, $BaCl_2 \cdot 2H_2O$, $ZnSO_4 \cdot 7H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Na_2S_2O_3 \cdot 5H_2O$, $NaC_2H_3O_2 \cdot 3H_2O$, $Na_3PO_4 \cdot 12H_2O$, $FeCl_3 \cdot 6H_2O$, $Cr_2(SO_4)_3 \cdot 18H_2O$, and $(CaSO_4)_2 \cdot H_2O$. Some anhydrous salts form no hydrates, while others form several. Under different conditions of temperature and vapor pressure, copper sulfate forms $CuSO_4 \cdot 5H_2O$, $CuSO_4 \cdot 3H_2O$, and $CuSO_4 \cdot H_2O$.

11. Numerous reactions, illustrating additional chemical properties of water, will be encountered in later chapters.

9.4 Vapor pressure of hydrates. Efflorescence. Deliquescence. Suppose at some definite and constant temperature, a few crystals of a pure hydrated salt, $BaCl_2 \cdot 2H_2O$ for example, are placed in a flask which contains dry, moisture-free air and which is fitted with a piston-like stopper that will enable the pressure on the flask to remain constant (see Figure 9.3). If the contents of the flask are observed with supermicroscopic eyes that can see individual molecules the following phenomena will, it is believed, be noted. The hydrate will immediately

begin to dissociate (decompose) into $BaCl_2$ and 2 H_2O, and molecules of water vapor (gas) will escape into the dry air at a *constant rate per unit* (per square centimeter or square inch) *of solid hydrate surface.* This rate

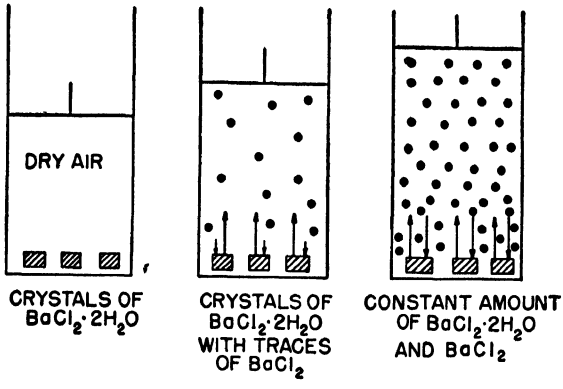


Figure 9.3. Attainment of the equilibrium, $BaCl_2 \cdot 2H_2O$ (solid) $\rightleftarrows$ $BaCl_2$ (solid) + $2H_2O$ (vapor).

of escape of H_2O gas molecules will remain constant as long as the temperature remains constant. At the moment the solid $BaCl_2 \cdot 2H_2O$ is first introduced into the flask there will be no H_2O gas molecules present. As time goes on and the dissociation of the $BaCl_2 \cdot 2H_2O$ proceeds, the concentration of H_2O gas molecules increases. Just as soon as a few molecules of H_2O gas are present, an occasional one will hop back onto the solid, where it will combine with the solid $BaCl_2$ according to the reaction

$$BaCl_2 \text{ (solid)} + 2\,H_2O \text{ (gas)} = BaCl_2 \cdot 2H_2O \text{ (solid)}$$

As the concentration of H_2O gas molecules increases, the number that will hop back onto unit solid surface in a given length of time will increase. Finally the concentration will get so high that the rate at which H_2O gas molecules hop back onto the surface and combine with $BaCl_2$ to form $BaCl_2 \cdot 2H_2O$ is equal to the constant rate at which H_2O molecules escape from the solid $BaCl_2 \cdot 2H_2O$. When that happens there will be no further increase in the concentration of H_2O gas molecules in the flask. The $BaCl_2 \cdot 2H_2O$ will keep right on dissociating into $BaCl_2$ and 2 H_2O at a constant rate, the H_2O molecules will keep right on hopping back onto the solid at the same rate, and the process will keep on going round and round; it will keep right on going forever, without stopping, at the same rate, if the temperature and pressure remain constant. The system is in a state of *equilibrium;* the *rate* at which $BaCl_2 \cdot 2H_2O$ is dissociating into $BaCl_2$ and 2 H_2O is exactly the

same as the *rate* at which $BaCl_2$ and $2\,H_2O$ are combining to form $BaCl_2 \cdot 2H_2O$. We can designate this state of equilibrium by the use of double arrows in the equation

$$BaCl_2 \cdot 2H_2O \rightleftarrows BaCl_2 + 2\,H_2O$$

The physical evidence that $BaCl_2 \cdot 2H_2O$ has decomposed and that $BaCl_2$ has been formed is the fact that some of the crystals of $BaCl_2 \cdot 2H_2O$ have been replaced by noncrystalline, powdered $BaCl_2$. It is assumed that enough $BaCl_2 \cdot 2H_2O$ was placed in the flask in the first place so that excess hydrate is present when equilibrium is established.

We have stated that, when equilibrium is reached, the concentration of H_2O gas molecules will then become constant; that means that the gas in the flask will contain a definite per cent of H_2O and a definite per cent of air. These H_2O molecules will exert a definite pressure. This pressure is referred to as the *vapor pressure of the hydrate.*

If, after equilibrium has been established in the above system, the temperature is increased, the following changes will take place. The hydrate will now dissociate at a faster constant rate. Although the H_2O gas molecules will move faster as a result of the increase in temperature and will accordingly hop back onto the solid at a slightly faster rate, they still will not return as fast as other H_2O molecules are escaping. As a result, the concentration of H_2O gas molecules will increase, the *partial pressure* due to these H_2O molecules will increase, and the rate at which H_2O gas reacts with $BaCl_2$ to form $BaCl_2 \cdot 2H_2O$ will increase. Finally the concentration will become so high that the rate at which the H_2O molecules return will again equal the rate at which they escape and equilibrium will again be established; the vapor pressure will, however, be higher than it was at the lower temperature. If this experiment were repeated with many hydrates at many temperatures we would find that *every hydrate exerts a definite vapor pressure at a definite temperature* and that *the vapor pressure of a hydrate increases as the temperature increases.* As a rule the pressure differs for different hydrates, but it is possible that two different hydrates may exert the same vapor pressure at a certain temperature. It should be noted that the product formed when a hydrate decomposes may be a hydrate with a lesser amount of water rather than an anhydrous salt. The equilibrium picture will, however, be the same as when an anhydrous salt is formed.

If, at a definite temperature, a hydrate is placed in an atmosphere in which the partial pressure of the water vapor is *exactly the same* as the vapor pressure of the hydrate at that temperature, no change in the physical condition of the hydrate will take place, and for all practical purposes nothing will happen. However, equilibrium will immediately

exist; the hydrate will immediately dissociate at a constant rate and will immediately be re-formed at the same constant rate.

If at a definite temperature a hydrate is placed in an atmosphere in which the partial pressure of the water vapor is *less* than the vapor pressure of the hydrate it will decompose. If a hydrate decomposes when placed in the open air at *ordinary room temperature* it is said to *effloresce*, and the process is referred to as *efflorescence*. The efflorescence of the hydrate will continue until either the hydrate is completely decomposed into anhydrous salt (or lower hydrate) or the partial pressure of the water vapor in the atmosphere equals the vapor pressure of the hydrate.

If an anhydrous salt (or lower hydrate) is placed in an atmosphere in which the partial pressure of the water vapor is *greater* than the vapor pressure of the hydrate (or higher hydrate), water vapor from the atmosphere will combine with the anhydrous salt (or lower hydrate) to form the hydrated salt (or higher hydrate). This process is called *deliquescence* and the anhydrous salt is said to be *deliquescent*. The anhydrous salt will continue to *deliquesce* until either it has all been converted to the hydrate (or a solution of the hydrate) or the partial pressure of the water vapor in the atmosphere has been reduced to the vapor pressure of the hydrate. Deliquescent salts such as anhydrous $CaCl_2$ are used to reduce the humidity of the air.

9.5 Formation of water. Water is so plentiful that it is not necessary to prepare it on a commercial scale. It is however of scientific interest to note the reactions in which it is formed as a product.

1. *Burning of hydrogen in oxygen or air*

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

2. *Burning of hydrogen compounds in oxygen or air*

$$CH_4 \text{ (methane)} + 2\,O_2 = CO_2 + 2\,H_2O$$
$$C_6H_{10}O_5 \text{ (cellulose, wood)} + 6\,O_2 = 6\,CO_2 + 5\,H_2O$$

3. *Reduction of the oxides of metals by hydrogen*

$$CuO + H_2 \text{ (heated)} = Cu + H_2O$$
$$SnO_2 + 2\,H_2 \text{ (heated)} = Sn + 2\,H_2O$$

In general, the more reactive the metal, the more difficult its oxide is to reduce with hydrogen. The reduction of an oxide with hydrogen serves as an industrial method for preparing certain metals.

4. *Irreversible thermal decomposition of carbohydrates.* Carbohydrates are compounds containing carbon, hydrogen, and oxygen in which the

hydrogen and oxygen are present in the same ratio in which they are present in water, that is, in the ratio of 2 atoms of hydrogen to 1 atom of oxygen. The name *carbo-hydrate* is derived from this H-O ratio. The carbo*hydrates* are not hydrates in the sense that hydrates have been discussed earlier in this chapter; the H and O which they contain are not present as H_2O. They do, however, give off water when they are heated out of contact with air. This decomposition is *irreversible;* the water that is given off will not react with the carbon and/or other products that remain as a residue to re-form the carbohydrates. The following equations illustrate the simple decomposition of some typical carbohydrates to yield carbon and water.

$C_{12}H_{22}O_{11}$ (sucrose; cane sugar) + heat = 12 C + 11 H_2O

$C_6H_{12}O_6$ (glucose; dextrose; corn syrup) + heat = 6 C + 6 H_2O

$C_6H_{10}O_5$ (starch unit) + heat = 6 C + 5 H_2O

$C_6H_{10}O_5$ (cellulose unit) + heat = 6 C + 5 H_2O

It should be noted that the carbohydrates cited above do not always decompose in this simple manner when heated; much more complex reactions may, and do, take place under specific conditions.

5. *Numerous reactions which will be encountered later yield water as a product.*

9.6 Natural water. Pure water. Natural water as it occurs in oceans, lakes, streams, and wells always contains varying amounts of dissolved material. It is therefore never "pure" in the sense of being chemically pure; it always contains some impurities. It may, however, be classed as pure in the sense that it contains no harmful bacteria or other toxic material and is therefore safe to drink.

Since natural waters are solutions they will be discussed in detail in Chapter 11. Chemically pure water is primarily of scientific interest; it can be prepared by the reactions given in 9.5.

Questions and Problems

1. Describe all the tests, both physical and chemical, that you could use to prove that a certain liquid is chemically pure water.

2. Show, by a balanced chemical equation, the reaction, if any, which takes place when each of the following is added to cold water: Cs, SeO_2, SrO, NaH, Na_2O_2.

3. Give balanced equations for four reactions in which water is formed as a product.

4. Give balanced equations for four reactions in which H_2O functions as an oxidizing agent. In each reaction point out the reducing agent, the element oxidized, the element reduced, and the change in oxidation number of the element oxidized and the element reduced.

5. You are given the following substances: $KClO_3$, CuO, Zn, HCl, Mg, S. Show by a series of balanced equations how $MgSO_3$ can be prepared.

6. You are given the following substances: HgO, PbO, Na, Zn, P, H_2SO_4. Show by a series of balanced equations how each of the following can be prepared: NaOH; H_3PO_4.

7. Define or describe and illustrate each of the following: hydrate; water of hydration; water of crystallization; anhydrous salt; vapor pressure of a hydrate; efflorescence; deliquescence; carbohydrate.

8. Show by balanced chemical equations what happens when each of the following is heated:

(a) A mixture of Mg and water.
(b) Solid sugar, $C_{12}H_{22}O_{11}$.
(c) $BaCl_2 \cdot 2H_2O$.
(d) Steam (to 2500°C), in a closed container.
(e) A mixture of CuO and H_2.

9. An excess of solid hydrate is placed in a flask of dry air at room temperature. Point out exactly what happens.

10. An anhydrous salt which forms a stable hydrate is placed in a flask of moist air at room temperature. Point out exactly what happens.

11. Account for the fact that $Na_2CO_3 \cdot 10H_2O$ will effloresce in a lecture room at 70°F in midwinter but will not effloresce in the same room on an early fall day when the temperature of the room is still 70°F.

12. Crystals of a hydrated salt are kept in a small compartment at the top of a tobacco humidor to maintain a constant moisture content. Explain how the crystals function. What will happen to the moisture content of the tobacco if the temperature of the room rises from 70°F to 90°F? If it falls to 40°F?

13. A salt hydrate whose vapor pressure at 20°C is 10.1 mm of mercury was placed in an open dish at 20°C when the relative humidity of the air was 60%. What would happen to the salt? Explain.

14. A hydrated salt, placed in the open air at 25°C effloresced when the relative humidity was 20% but did not effloresce when the relative humidity was 25%. What is the approximate value of the vapor pressure of the hydrated salt at 25°C?

15. What must be the vapor pressure of a hydrate if it is to maintain a relative humidity of 80% in a tobacco humidor at 72°F?

16. Explain why:

(a) Water is observed to drip from the exhaust pipe of an automobile in cold weather.

(b) The glass chimney of a kerosene lamp or lantern clouds over when first lighted, but soon clears up.

(c) Heat is generated when water is added to lime (CaO) in the preparation of building mortar.

(d) Heat is generated when water is added to anhydrous $CuSO_4$.

(e) The freezing of entrained water causes rocks to be cracked.

(f) A burn resulting from contact with steam at 100°C is more severe than a burn by hot water at 100°C.

(g) Water has such a high boiling point by comparison with the boiling points of H_2S and H_2Se.

(h) Water boils at a lower temperature on Pikes Peak than in New Orleans.

(i) The water at the bottom of a lake never gets colder than 4°C.

(j) Ice at 0°C is a better cooling agent than water at 0°C.

(k) A goblet filled to the top with water and containing a large cube of ice which sticks up over the top of the water does not overflow when the ice melts.

(l) Pure water is a poor conductor of electric current.

(m) Water is such an effective cooling agent for use in automobile engines.

(n) The water in a lake "turns over."

17. How many moles of water will be formed by complete combustion of 3 moles of C_3H_8?

18. How many gram-atoms of Cu will be formed by reduction with hydrogen of 6 moles of CuO? How many grams of hydrogen will be required to accomplish the reduction? How many moles of steam will be formed?

19. How many liters of dry hydrogen gas, measured at STP, will be liberated by the reaction of 2 gram-atoms of calcium with an excess of water?

20. How many liters of oxygen gas will be required to burn 160 l of hydrogen gas, both gases being measured at 750 mm and 25°C?

21. An Arizona grocer bought 100 lb of hydrated washing soda, $Na_2CO_3 \cdot 10H_2O$, in sealed drums at 10 cents per pound. He transferred the material to an open bin for retail sale and found, before a single sale

could be made, that the hydrate had completely deliquesced to the anhydrous salt. At what price would he have to sell the anhydrous salt in order to realize a profit of 20% on his original investment?

22. Calculate the per cent of water of hydration in $ZnSO_4 \cdot 7H_2O$.

23. Two gram-formula weights of cellulose ($C_6H_{10}O_5$) were burned in air. How many grams of CO_2 were formed?

24. How many grams of water of crystallization are there in 150 g of $Na_3PO_4 \cdot 12H_2O$?

CHAPTER 10

Rate of Reaction and Equilibrium in Chemical Reactions

10.1 Factors that effect the rate of a reaction. We have already learned in Chapter 3 that the rate of a reaction depends upon:

1. *The reactivities of the reacting substances.* Some reactions are inherently rapid, some are inherently slow, some are over in a minute or a second, some require hours, days, or even years before they are completed. To account for this inherent difference in speed we say that some substances are very reactive, while others are relatively nonreactive. Thus, potassium reacts with HCl very rapidly, while tin reacts slowly; we account for this difference by saying that potassium is more *reactive* than tin. The exact reason why potassium is more reactive than tin need not concern us at this point.

2. *The temperature.* Whether a reaction is inherently slow or rapid, its rate will increase if the temperature is raised and will decrease if the temperature is lowered. For the average reaction the rate will just about double for every 10 deg centigrade increase in temperature. Before 2 molecules can react with each other they must actually collide. Increasing the temperature increases the rate at which molecules move, and therefore increases the number of times that they will collide per second. This will increase the rate of reaction. More significant, however, in its effect on the rate is the fact that increase in temperature causes a greater per cent of the colliding molecules to react with each other. Not all the colliding molecules will react with each other; only the "active" or "hot" ones will do so. Increasing the temperature increases greatly the per cent of these "active" molecules.

3. *The presence of a catalyst.* As has already been noted, a catalyst speeds up (or, in rare cases, slows down) a reaction without apparently being affected or changed. Thus MnO_2 catalyzes the rate of decomposition of $KClO_3$, and platinum catalyzes the rate of reaction between H_2 and O_2. Although there is a great deal of speculation and question about how a specific catalyst functions when it alters the speed of a reaction, it seems a pretty well-established fact that a catalyst cannot initiate a

reaction. All it can do is speed up a reaction that is already proceeding at a finite rate. It probably accomplishes this speed-up because it provides a different or easier path or mechanism for the reaction to follow.

4. *The concentrations of the reacting substances.* Whether a reaction is inherently slow or inherently rapid, increasing the concentration of a reactant will increase its speed. To illustrate, we observed that a splint burns faster in pure oxygen than it does in air, which is only 20% oxygen by volume. Iron, we found, burns slowly in air but burns rapidly in pure oxygen. Magnesium burns rapidly in air; it burns more rapidly in pure oxygen. As already noted, oxygen molecules must actually collide with a piece of magnesium before a reaction can take place. The rate of the reaction will depend on the number of oxygen molecules that collide with the piece of magnesium per second. The greater the number of oxygen molecules that are present in a given volume in a flask for example, the greater will be the number that will collide with the magnesium per second and the faster will be the rate of the reaction. Concentration, it should be recalled, means the quantity of material per unit volume. Therefore, increasing the number of oxygen molecules in a given volume means increasing the concentration of the oxygen. We can state, therefore, that the rate at which magnesium burns increases when the concentration of the oxygen increases. As a general rule *the rate of any reaction increases when the concentration of a reactant is increased.* That means that *the rate of a reaction is proportional to the concentrations of the reacting substances.*

10.2 Reversible reactions. Equilibrium. Our attention has already been called to reactions in which the products react with each other to form the initial reactants (or reactant). These reactions eventually reach a *state of equilibrium.* At equilibrium, the rates of the forward and reverse reactions are the same and the reaction keeps on going round and round without there being any further change in the amounts of the reactants and products. Such reactions are said to be *reversible* or *incomplete;* some typical examples that have been cited earlier in this book are

$$Zn + H_2O \rightleftarrows ZnO + H_2$$

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

$$BaCl_2 \cdot 2H_2O \text{ (solid)} \rightleftarrows BaCl_2 \text{ (solid)} + 2\,H_2O \text{ (vapor)}$$

In each of these reactions it is found, experimentally, that the same state of equilibrium is reached whether we start with the substances on the right or on the left. Thus if a mixture of H_2 and ZnO is heated in a closed container, the equilibrium $ZnO + H_2 \rightleftarrows Zn + H_2O$ will be estab-

lished, while if a mixture of Zn and H_2O is heated, the same equilibrium $Zn + H_2O \rightleftarrows ZnO + H_2$ will be set up. Likewise a mixture of H_2 and O_2, heated to a high temperature, will give the equilibrium $2\,H_2 + O_2 \rightleftarrows 2\,H_2O$ just as steam, heated to the same temperature will give the same equilibrium $2\,H_2O \rightleftarrows 2\,H_2 + O_2$. *It is characteristic of every true equilibrium reaction that the same state of equilibrium will be reached by starting with either the reactants or the products.*

It should be noted that it is not a requirement of equilibrium that the substances be present in the reaction vessel in the exact ratio in which they combine. Thus if a mixture of 10 moles of oxygen and 6 moles of hydrogen is heated to 2000°C, the equilibrium $2\,H_2 + O_2 \rightleftarrows 2\,H_2O$ will be set up just as surely as if a mixture of 4 moles of oxygen and 6 moles of hydrogen is heated. The amounts of H_2, O_2, and H_2O present in the first equilibrium mixture will not be the same as the amounts present in the second mixture, but in both mixtures a state of equilibrium is attained. The substances will *react* with each other in the mole ratio represented by the equation for the reaction but they can be present in the reaction vessel in all sorts of ratios.

10.3 The equilibrium constant. The statement was made, in Section 10.2, that in a reaction vessel in which the equilibrium represented by the reaction $2\,H_2 + O_2 \rightleftarrows 2\,H_2O$ existed, the H_2, O_2, and H_2O could be present in all sorts of ratios even though they interact in the exact ratio represented by the equation. The same statement applies to all equilibrium reactions. If we were to measure the exact concentrations, in moles per liter, of the four reactants, CO, H_2O (steam), CO_2, and H_2, present in each of 5 *one-liter* reaction vessels, *all at the same temperature*, in which the equilibrium $CO + H_2O$ (steam) $\rightleftarrows CO_2 + H_2$ existed, we could obtain results such as those given in Table 10.1.

TABLE 10.1

RELATIVE CONCENTRATIONS OF REACTANTS IN AN EQUILIBRIUM SYSTEM AT CONSTANT TEMPERATURE

Reaction vessel	[CO]	[H_2O]	[CO_2]	[H_2]	$\frac{[CO_2] \times [H_2]}{[CO] \times [H_2O]}$
1	0.20	0.20	0.50	0.40	5.00
2	0.10	0.18	0.30	0.31	5.16
3	0.10	0.80	0.80	0.50	5.00
4	0.30	0.50	0.90	0.83	4.98
5	0.75	0.20	0.80	0.94	5.01

The notations [CO], [H_2O], [CO_2], and [H_2] mean concentration in moles per liter of the substance within the bracket.

An examination of the data in the table reveals the striking fact that in every vessel the product of the concentrations of the products (CO_2 and H_2) divided by the product of the concentrations of the reactants (CO and H_2O) always equals the same constant value, 5. The variations from 5 (5.16, 5.01, and 4.98) lie within the limits of experimental error. If we were to repeat the experiment with a great many different equilibrium systems we would find, in every case, that, *at constant temperature, the product of the concentrations of the products divided by the product of the concentrations of the reactants is constant.* The numerical value of the constant will vary from one equilibrium reaction to the next, but for any specific reaction at a specific temperature the same constant is always obtained. For a specific reaction, however, a different constant is obtained at a different temperature; for some reactions the value of the constant is increased when the temperature is increased, for others it is decreased. The constant value is referred to as the *equilibrium constant* for the particular reaction at the particular temperature, and is represented by the symbol K. Expressed in the form of a mathematical equation, for the reaction $CO + H_2O \rightleftarrows CO_2 + H_2$,

$$K = \frac{[CO_2] \times [H_2]}{[CO] \times [H_2O]}$$

For the reaction $SO_2 + NO_2 \rightleftarrows SO_3 + NO$,

$$K = \frac{[SO_3] \times [NO]}{[SO_2] \times [NO_2]}$$

When a reaction involves more than 1 mole of a specific reactant, the concentration of that reactant is raised to a power equal to the number of moles. Thus for the reaction $2\,SO_2 + O_2 \rightleftarrows 2\,SO_3$,

$$K = \frac{[SO_3]^2}{[SO_2]^2 \times [O_2]}$$

For the reaction $N_2 + 3\,H_2 \rightleftarrows 2\,NH_3$,

$$K = \frac{[NH_3]^2}{[N_2] \times [H_2]^3}$$

and for the reaction $H_2 + I_2 \rightleftarrows 2\,HI$,

$$K = \frac{[HI]^2}{[H_2] \times [I_2]}$$

The reason for raising the concentration of a reactant to a power equal to the number of moles becomes more evident if we show each mole as a separate reactant by writing the equation for the reaction in the form

$$N_2 + H_2 + H_2 + H_2 \rightleftarrows NH_3 + NH_3$$

The equilibrium constant, K, can then be expressed in the form

$$K = \frac{[NH_3] \times [NH_3]}{[N_2] \times [H_2] \times [H_2] \times [H_2]} = \frac{[NH_3]^2}{[N_2] \times [H_2]^3}$$

Equilibrium constants have been determined experimentally for hundreds of reactions and are listed in reference books such as the *International Critical Tables. Every* equilibrium reaction has its own equilibrium constant.

10.4 Shifting the equilibrium in a reversible reaction. The equilibrium in a reaction may be shifted:

1. *By changing the concentration of a reactant.* Since the rate of a reaction is proportional to the concentration of the reacting substances, it follows that if, in a system in equilibrium, the concentration of a specific reactant is changed, the rate of the reaction in which that particular reactant is involved will be changed. As a result, the relative amounts of all substances involved in the reaction will be changed. This change in the relative amounts of all reactants as a result of increasing or decreasing the concentration of a reactant is commonly referred to as a *shifting of the equilibrium.*

To illustrate, suppose the reaction $SO_2 + NO_2 \rightleftarrows SO_3 + NO$ has reached a state of equilibrium at a definite temperature in a liter reaction flask. An analysis of the equilibrium mixture shows, let us say, that it contains 0.4 mole of SO_3, 0.4 mole of NO, 0.3 mole of NO_2, and 0.3 mole of SO_2. Now suppose we increase the concentration of the nitric oxide, NO, by forcing more of it into the reaction vessel. Since the rate at which NO reacts with SO_3 is proportional to the concentration of NO, it follows that the rate of the reaction of NO with SO_3 (the rate of the reaction to the left) will be speeded up. As a result, SO_2 and NO_2 will be formed at a faster rate than before the excess NO was added. Whereas, at equilibrium, the SO_2 and NO_2 were reacting to give SO_3 and NO at the same rate as the SO_3 and NO were reacting to give SO_2 and NO_2, it is true that they are now being formed faster than they are reacting to form SO_3 and NO. The net result is that the quantity of SO_2 and NO_2 in the reaction vessel will increase. To produce this increased quantity of SO_2 and NO, some of the SO_3 originally present in the vessel at equilibrium must have been used up. A new equilibrium will eventually be set up, but at this new equilibrium, the amount of SO_2 and NO_2 in the liter flask will be greater, and the amount of SO_3 will be less than in the original equilibrium system. Since the volume of the reaction flask

remains constant at 1 liter the concentration of the SO_2 and NO_2 has increased, while the concentration of the SO_3 has decreased. Since NO was added to the system, its concentration must obviously have increased even though some NO must have reacted with the SO_3 to produce the increased amounts of SO_2 and NO_2. If we use different size type to represent different concentrations of substances we can pictorialize what has taken place as follows:

Original equilibrium:

$$SO_2 + NO_2 \rightleftarrows SO_3 + NO$$

Final equilibrium, after addition of NO:

$$\mathbf{SO_2 + NO_2 \rightleftarrows SO_3 + NO}$$

Since the concentrations of all substances on the left have increased, we say that the equilibrium has been shifted to the left. Had we increased the concentration of either the SO_2 or the NO_2, the equilibrium would have been shifted to the right. Addition of more SO_3 would have shifted the equilibrium to the left. A simple rule to follow in determining the equilibrium shift is this: if the concentration of a reactant on the left side of the equation is increased, the equilibrium will be shifted to the right, while if the concentration of a reactant on the right side of the equation is increased the equilibrium will be shifted to the left.

The equilibrium can also be shifted by removing a quantity of a reactant (reducing its concentration). This obviously will lower the rate of the reaction in which that reactant is involved, and will shift the equilibrium in the direction opposite to that in which it will be shifted if the concentration is increased. The over-all rule covering both increase and decrease in concentration is: if a reactant on the left is *added*, the equilibrium will be *pushed* to the right; if a reactant on the left is *removed*, the equilibrium will be *pulled* to the left; the same argument holds for a reactant on the right.

It is important to remember that, in all this equilibrium shifting, at constant temperature, the value of the equilibrium constant for the reaction does not change. At each new equilibrium, the product of the concentrations of the products divided by the product of the concentrations of the reactants is equal to the same constant. The only way to change the value of the equilibrium constant is to change the temperature.

The calculation of the quantitative effect on an equilibrium reaction of increase and decrease in the concentration of a reactant is discussed in Section 10.5.

The quantitative relationship between the rate of a reaction and the

concentrations of the reactants was enunciated by the Norwegian scientists Guldberg and Waage in 1867, when they concluded that *the rate of a reaction is proportional to the product of the concentrations of the reacting substances*. This generalization is known as the *law of mass action;* a detailed discussion of the mass law and reaction rates is beyond the scope of this book.

2. *By changing the temperature.* The effect of a change in temperature on an equilibrium will depend on whether the reaction in a given direction is exothermic or endothermic. Suppose the reaction A + B = C + D takes place with evolution of heat (is exothermic). That means that the reverse reaction C + D = A + B takes up heat (is endothermic). These facts can be represented by the equation

$$A + B \rightleftarrows C + D + \text{heat}$$

Addition of heat will favor the reaction which absorbs heat. Therefore addition of heat (increasing the temperature) will speed up the reaction to the left. As a result the equilibrium will be shifted to the left. Removal of heat (lowering the temperature) will have the opposite effect; it will slow down the reaction which absorbs heat, and will therefore shift the equilibrium to the right.

An increase in temperature will, according to the above rule, shift the following equilibria to the left:

$$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3 + \text{heat}$$
$$2\ NO_2 \rightleftarrows N_2O_4 + \text{heat}$$
$$H_2 + Cl_2 \rightleftarrows 2\ HCl + 22{,}000\ \text{cal}$$

The following equilibria will be shifted to the right by a temperature increase. (Removal of heat on the right is equivalent to addition of heat on the left.)

$$H_2 + I_2 \rightleftarrows 2\ HI - 6200\ \text{cal}$$
$$PCl_5 \rightleftarrows PCl_3 + Cl_2 - 22{,}130\ \text{cal}$$
$$2\ P + 3\ H_2 \rightleftarrows 2\ PH_3 - 2210\ \text{cal}$$

As already noted, change in temperature will change the numerical value of the equilibrium constant for a specific reaction.

3. *By changing the pressure.* A change in the total pressure on an equilibrium reaction system will change the equilibrium: (a) if one or more of the reactants or products are gases; and (b) if the number of moles of gaseous reactants is different from the number of moles of gaseous products.

Under these conditions, increase in pressure will shift the equilibrium toward that side which has the smaller number of moles of gas.

This shift takes place in accordance with the principle of Le Chatelier, which states that if a system in equilibrium is subjected to a stress or strain that change will take place which tends to relieve the stress or strain. Thus if pressure is increased on the equilibrium system represented by the reaction

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

the equilibrium will be shifted to the right. There are 4 moles of gaseous reactants on the left and only 2 moles on the right. Two moles of gas exert only half the pressure of 4 moles. Therefore a shift to the right, toward the formation of NH_3, will relieve the pressure stress. The equilibrium of the following gas phase reactions will all be shifted to the right by a pressure increase.

$$2\ SO_2 + O_2 \rightleftarrows 2\ SO_3$$
$$2\ H_2 + O_2 \rightleftarrows 2\ H_2O$$
$$PCl_3 + Cl_2 \rightleftarrows PCl_5$$

The following equilibria will be shifted to the left by a pressure increase.

$$CaCO_3\ (\text{solid}) \rightleftarrows CaO\ (\text{solid}) + CO_2\ (\text{gas})$$
$$NH_4Cl\ (\text{gas}) \rightleftarrows NH_3\ (\text{gas}) + HCl\ (\text{gas})$$
$$COCl_2 \rightleftarrows CO + Cl_2\ (\text{all gases})$$

The commercial preparation of sulfur trioxide by the contact process ($2\ SO_2 + O_2 \rightleftarrows 2\ SO_3$) and that of ammonia by the Haber process ($N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$) are both carried out at high pressures since this shifts the equilibria in the direction of maximum yield of the desired products.

The equilibrium in a reaction such as

$$NO_2 + SO_2 \rightleftarrows NO + SO_3$$

is not altered by a change of pressure because the numbers of moles (total volume) of reactants and products are equal.

Change in pressure, at constant temperature, does not change the value of the equilibrium constant; as already noted, the only way to do that is to change the temperature.

4. *A catalyst does not alter the equilibrium of a reaction.* It speeds up, to an equal extent, the rates of the forward and reverse reactions. It therefore speeds up the rate at which equilibrium is attained but has no effect on the equilibrium point.

10.5 Calculation of the effect of change in concentration on the equilibrium. The magnitude of the change produced when the concentration of a

reactant in an equilibrium system is changed can be calculated by the use of the formula representing the equilibrium constant of the reaction. To illustrate, suppose we are asked to solve the following problem: The equilibrium mixture, $SO_2 + NO_2 \rightleftarrows SO_3 + NO$, in a liter vessel, was found to contain 0.6 mole of SO_3, 0.4 mole of NO, 0.1 mole of NO_2, and 0.8 mole of SO_2. How many moles of NO would have to be forced into the reaction vessel, volume and temperature being kept constant, in order to increase the concentration of NO_2 to 0.3 mole?

Solution: First calculate the equilibrium constant.

$$K = \frac{[SO_3] \times [NO]}{[SO_2] \times [NO_2]} = \frac{0.6 \times 0.4}{0.8 \times 0.1} = 3$$

Let X = moles of NO that must be added. We can see, from the equation $SO_2 + NO_2 \rightleftarrows SO_3 + NO$ that in order to produce 0.2 more mole of NO_2 we must also produce 0.2 more mole of SO_2, and we must use up 0.2 mole of SO_3 and 0.2 mole of NO. Therefore when we have 0.3 mole of NO_2, we will have 1 mole $(0.8 + 0.2)$ of SO_2, 0.4 mole $(0.6 - 0.2)$ of SO_3, and $X + 0.2$ mole $(0.4 + X - 0.2)$ of NO. Substituting the values in the equilibrium formula, we have

$$\frac{0.4 \times (X + 0.2)}{1 \times 0.3} = 3; \qquad X = 2 \text{ moles}$$

In reviewing the above calculation it should be noted that:

(a) It is not necessary that the number of moles of SO_2 in the vessel be the same as the number of moles of NO_2 or that the number of moles of SO_3 be the same as the number of moles of NO. Practically any number of moles of SO_2, NO_2, SO_3, and NO can be introduced into the reaction vessel; they will react and the reaction will be reversible and will adjust itself until the product of $[SO_3]$ times [NO] divided by the product of $[SO_2]$ times $[NO_2]$ equals the equilibrium constant K for the reaction.

(b) When SO_2 reacts with NO_2, or SO_3 reacts with NO, they always interact in the mole ratio represented by the equation. Every time 1 mole of SO_2 is formed, 1 mole of NO_2 is also formed; and every time a new mole of SO_2 is formed, 1 mole of SO_3 and 1 mole of NO are used up. In other words, the SO_2, NO_2, SO_3, and NO need not be *present* in the mole ratio represented by the equation, but when they *react* they always do so in that exact mole ratio.

10.6 Complete reactions. If one of the reactants in an equilibrium reaction system is removed so that it has no chance to continue to take part in the reaction, the equilibrium will be destroyed and the reaction will go on to completion. To illustrate: if some solid copper oxide is dropped into a flask in which the reaction $N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$ is in an equilibrium state, the CuO will immediately react with the H_2 to form Cu and H_2O according to the equation $CuO + H_2 = Cu + H_2O$. If sufficient CuO is added, it will react with all the hydrogen; not only will it react with the hydrogen that is present at the moment, but it will pick

off the hydrogen molecules as fast as they are formed by decomposition of the NH_3 in the flask. The net result will be that the reaction of N_2 with H_2 will stop. Since NH_3 is no longer being formed, the ammonia content of the flask will eventually be reduced to zero. Stated briefly, the CuO removes the H_2 and thereby causes the reaction to be *complete* to the left. A *complete reaction* may be defined as one which, at the time of the experiment, goes in only one direction.

In numerous instances that will be encountered later in this book, *removal from solution of reaction products in the form of insoluble gases or insoluble solid precipitates* reduces the concentration of a reactant to such a low value that, for all practical purposes, the reaction is complete and no equilibrium is established. The following equations represent typical examples.

$$2\ NaCl\ (\text{dry solid}) + H_2SO_4\ (\text{concentrated}) = Na_2SO_4 + 2\ HCl\uparrow \quad (\text{gas escapes})$$

$$Na_2CO_3\ (\text{solution}) + 2\ HCl\ (\text{solution}) = 2\ NaCl\ (\text{solution}) + H_2O + CO_2\uparrow \quad (\text{gas escapes})$$

$$AgNO_3\ (\text{solution}) + NaCl\ (\text{solution}) = NaNO_3\ (\text{solution}) + AgCl\downarrow \quad (\text{precipitate})$$

$$BaCl_2\ (\text{solution}) + Na_2SO_4\ (\text{solution}) = 2\ NaCl\ (\text{solution}) + BaSO_4\downarrow \quad (\text{precipitate})$$

Detailed interpretation of these reactions will be given in later chapters.

Reactions in which one element replaces a less active element from a compound are complete because the displaced element is not, under ordinary conditions, able to turn around and displace the displacing element. Examples of reactions of this type are:

$$2\ Na + 2\ H_2O = 2\ NaOH + H_2$$

$$Mg + 2\ HCl = MgCl_2 + H_2$$

$$Zn + CuSO_4 = ZnSO_4 + Cu$$

$$Cl_2 + 2\ KBr = 2\ KCl + Br_2$$

It should be noted that, under proper conditions which need not concern us at this time, these replacement reactions are reversible. There are, however, a few reactions that are *irreversible* as well as complete; the products cannot, under any known condition, be made to react to re-form the initial reactant or reactants. Examples of such reactions are:

$$C_{12}H_{22}O_{11}\ (\text{sucrose}) + \text{heat} = 12\ C + 11\ H_2O$$

$$2\ KClO_3 + \text{heat} = 2\ KCl + 3\ O_2$$

$$PCl_3 + 3\ H_2O = H_3PO_3 + 3\ HCl$$

Questions and Problems

1. Define or describe and illustrate: reversible reaction; equilibrium; concentration; complete reaction; incomplete reaction; irreversible reaction; principle of Le Chatelier; equilibrium constant.

2. List the factors which will effect the rate of a reaction.

3. List the factors which can change the equilibrium in a reaction and point out how each factor operates.

4. Point out the conditions under which a reaction will be complete or practically complete.

5. Give a detailed word picture of the process whereby equilibrium is attained when a mixture of SO_2 and NO_2 reacts according to the equation $SO_2 + NO_2 \rightleftarrows SO_3 + NO$. Give a detailed word picture of exactly what happens when NO gas is forced into the reaction vessel in which the above equilibrium exists.

6. Given the gas phase reaction $N_2 + 3\ H_2 \rightleftarrows 2\ NH_3 + 24{,}000$ cal, at equilibrium in a closed container at 500°C. How would the equilibrium be influenced by:

(a) Increasing the temperature?
(b) Increasing the pressure?
(c) Introducing some platinum catalyst?
(d) Forcing more H_2 gas into the system?
(e) Forcing more N_2 gas into the system?
(f) Adding an excess of solid CuO?
(g) Lowering the temperature to 300°C?

7. In industrial preparation of ammonia by the reaction given in question 6, a temperature of 500°C is maintained. Why not run the reaction at 300°C?

8. How will an increase in pressure effect the equilibrium in each of the following gas phase reactions?

(a) $H_2 + I_2 \rightleftarrows 2\ HI$
(b) $4\ NH_3 + 5\ O_2 \rightleftarrows 4\ NO + 6\ H_2O$ (steam)
(c) $PCl_3 + Cl_2 \rightleftarrows PCl_5$
(d) $2\ H_2 + O_2 \rightleftarrows 2\ H_2O$ (steam)

9. How will an increase in temperature effect each of the following reactions?

(a) $2\ NO_2 \rightleftarrows N_2O_4 +$ heat
(b) $H_2 + Cl_2 \rightleftarrows 2\ HCl + 22{,}000$ cal
(c) $H_2 + I_2 \rightleftarrows 2\ HI - 6000$ cal

10. At equilibrium at a given temperature and in a liter reaction vessel, HI is 20 mole per cent dissociated into H_2 and I_2 according to the equation $2\ HI \rightleftarrows H_2 + I_2$. If 1 mole of pure HI is introduced into a liter reaction vessel at the given temperature, how many moles of each component will be present when equilibrium is established?

11. The compound PCl_5 is 20 mole per cent dissociated into PCl_3 and Cl_2 at equilibrium at a given temperature and in a liter vessel, in accordance with the equation $PCl_5 \rightleftarrows PCl_3 + Cl_2$. One mole of pure PCl_5 was introduced into a liter reaction vessel at the given temperature. How many moles of each component were present at equilibrium?

12. A reaction vessel in which the reaction $CO + Cl_2 \rightleftarrows COCl_2$ had reached a state of equilibrium was found, on analysis, to contain 0.300 mole of CO, 0.200 mole of Cl_2, and 0.800 mole of $COCl_2$, in a liter of mixture. Calculate the equilibrium constant.

13. A reaction vessel with a capacity of 1 l in which the reaction $2\ SO_2 + O_2 \rightleftarrows 2\ SO_3$ had reached a state of equilibrium was found to contain 0.60 mole of SO_3, 0.20 mole of SO_2, and 0.30 mole of O_2. Calculate the equilibrium constant.

14. The equilibrium constant for the reaction $CO + H_2O \rightleftarrows CO_2 + H_2$ is 4.0 at a given temperature. An equilibrium mixture of the above substances at the given temperature was found to contain 0.60 mole of CO, 0.20 mole of steam, and 0.50 mole of CO_2 in a liter. How many moles of H_2 were there in the mixture?

15. An equilibrium mixture, $CO + H_2O \rightleftarrows CO_2 + H_2$, contains 0.2 mole of H_2, 0.8 mole of CO_2, 0.1 mole of CO, and 0.4 mole of H_2O in a liter. How many moles of CO_2 would have to be added at constant temperature and volume to increase the concentration of CO to 0.2 mole?

16. An equilibrium mixture, $SO_2 + NO_2 \rightleftarrows SO_3 + NO$, contains 0.6 mole of SO_3, 0.3 mole of NO, 0.6 mole of SO_2, and 0.1 mole of NO_2 in a liter. How many moles of SO_2 would have to be removed from the system in order to reduce the concentration of NO to 0.2 mole, volume and temperature being kept constant?

17. At a given temperature a liter reaction vessel contained 0.60 mole of $COCl_2$, 0.30 mole of CO, and 0.10 mole of Cl_2. $CO + Cl_2 \rightleftarrows COCl_2$. An amount of 0.40 mole of Cl_2 was added to the vessel at constant temperature and pressure. Calculate the number of moles of CO, Cl_2, and $COCl_2$ in the new equilibrium system.

18. The equilibrium constant for the reaction $CO + H_2O \rightleftarrows CO_2 + H_2$ is 4.0 at a given temperature. A combination of 0.40 mole of CO and 0.60 mole of steam was brought together in a liter vessel at this temperature. How many moles of CO_2 were present when the system reached a state of equilibrium?

CHAPTER 11

Solutions

11.1 Nature of a solution. If a small quantity of sugar is dropped into a beaker of water it will soon disappear. We say that it has *dissolved* and that a *solution* of sugar in water has been formed. The solution will be observed to be *homogeneous;* no particles of sugar can be seen. The sugar is referred to as the *solute;* it is the substance that is dissolved. The water is referred to as the *solvent;* it is the substance that does the dissolving. If more sugar is added, a small quantity at a time, to the solution just prepared, it will continue to dissolve. Finally, however, the solution will be unable to dissolve any more sugar; this will be indicated by the fact that crystals that are added will drop to the bottom of the beaker and will not dissolve even though the contents of the beaker are well stirred. A solution which has dissolved all the solute that it is capable of holding at a given temperature (as indicated by the presence of excess solute) is *saturated;* a solution which is capable of dissolving more solute at a given temperature is *unsaturated.*

The fact that the quantity of solute that is dissolved in a given amount of solvent may vary continuously all the way from a tiny bit to the larger amount required to give a saturated solution means that the composition of the solution is variable; therefore it is a mixture; it may be described correctly as a *homogeneous mixture.*

11.2 Physical state of solute and solvent. The solute in a solution may be a solid, a liquid, or a gas. Likewise the solvent may be a solid, a liquid, or a gas. Liquid and solid solvents can dissolve either solid, liquid, or gaseous solutes. A gaseous solvent can dissolve only gaseous solutes; it cannot dissolve solids or liquids. The substances that function as solute and solvent in a solution are referred to as its *components.*

Air is a solution of oxygen in nitrogen; it contains also small amounts of the gaseous components water vapor, carbon dioxide, argon, helium, neon, krypton, and xenon.

Natural water is a solution in which liquid water is the solvent and small amounts of gaseous air and various solid salts are the solutes.

Liquid methyl alcohol (CH_3OH) or liquid ethylene glycol

($HOCH_2CH_2OH$) is commonly dissolved in water to give a nonfreezing solution for use in automobile radiators.

Corn syrup is a solution of glucose ($C_6H_{12}O_6$) in water, while the brine solution used in commercial refrigeration systems is a solution of common salt (NaCl, sodium chloride) in water.

Brass is a solution of solid zinc in solid copper. Gaseous hydrogen will dissolve in solid palladium; liquid mercury will dissolve in solid zinc.

The solutions commonly used in general chemistry are those in which a solid, a liquid, or a gas is dissolved in a liquid; the other types are rarely encountered and will therefore not be given further consideration in this chapter.

11.3 Equilibrium in a saturated solution. If a quantity of crystals of sugar (more than enough to give a saturated solution) is placed in a beaker of water at a definite constant temperature and the system is observed with supermicroscopic eyes that can see molecules, the following behavior will, it is believed, be noted (see Figure 11.1). Molecules

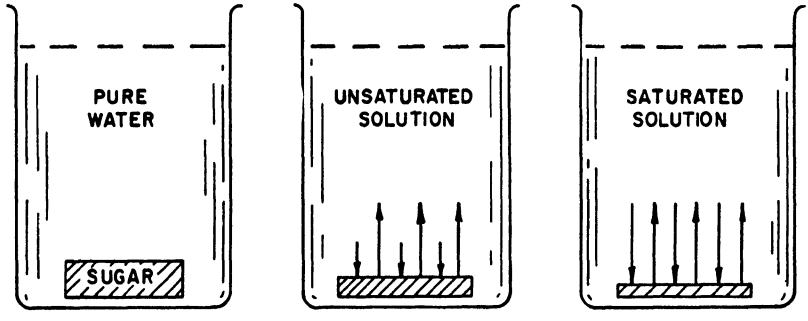


Figure 11.1. Equilibrium in a saturated solution of sugar in water.

of sugar will immediately start moving from the surface of the solid crystal into the water at a definite and constant rate per unit of surface area. This movement of molecules of sugar from the surface of the solid will continue without interruption and at the same constant rate. Just as soon as a few molecules of sugar get into solution an occasional one will hop back onto the crystal. As time goes on and the number of molecules of sugar in solution increases, the number that hop back on unit surface in a given length of time increases. Finally the concentration of the sugar in solution will reach the point where the molecules will hop back out of solution onto the crystal exactly as fast as they pass from the crystal into solution. When that point is reached there will be no further increase in the concentration of the molecules in solution.

The solid solute will then be in *equilibrium* with the solution, and the solution will be *saturated.* It can be stated, therefore, that *a saturated solution is in equilibrium with excess solute.* If the excess solute is carefully removed from the saturated solution the latter will still be saturated.

11.4 Solubility. The quantity of solute that will dissolve in a definite quantity of solvent to give a saturated solution is referred to as the *solubility* of the solute in the solvent. Solubility of a solid, liquid, or gas in a liquid is generally expressed in units of grams of solute per 100 g of solvent or grams of solute per 100 ml (or 100 cc) of solvent. Solubility of gases in liquids is commonly expressed in units of liters or cubic centimeters of gas per 100 g (or 100 ml or liter) of solvent.

The exact weight of solute (NaCl, for example) that will dissolve in 100 g or 100 ml of the solvent water can be determined in one of the following ways: (a) A weighed amount of NaCl is added to exactly 100 ml or exactly 100 g of water in a flask at 20°C and the mixture is shaken until a saturated solution is obtained. The excess NaCl is then filtered off, dried, and weighed. The difference between the weight of the NaCl added to the flask and the weight of the excess NaCl gives the solubility in grams of NaCl per 100 g or 100 ml of water. (b) A saturated solution at 20°C is first prepared by adding excess NaCl to an indefinite volume of water (25–100 ml) in a flask. A quantity of this saturated solution (10–15 g, let us say) is transferred to a clean, dry, flask whose exact weight is known. The exact weight of the flask and saturated solution is then determined; the exact weight of the saturated solution is then calculated by difference. The saturated solution in the weighed

TABLE 11.1

DETERMINATION OF THE SOLUBILITY OF NaCl IN WATER AT 20°C

(1)	Weight of flask	61.024 g
(2)	Weight of flask + saturated solution	75.985 g
(3)	Weight of saturated solution, (2) − (1)	14.961 g
(4)	Weight of flask + dry salt	64.985 g
(5)	Weight of dry salt, (4) − (1)	3.961 g
(6)	Weight of water, (3) − (5)	11.000 g
(7)	Density of water at 20°C	0.9982 g/cc
(8)	Volume of the 11.000 g of water	11.020 cc
(9)	Calculated solubility	36.010 g/100 g of water
	$\frac{3.961 \text{ g of NaCl}}{11.000 \text{ g of water}} = \frac{36.010 \text{ g of NaCl}}{100.000 \text{ g of water}}$	
(10)	Calculated solubility	35.944 g/100 cc of water
	$\frac{3.961 \text{ g of NaCl}}{11.020 \text{ cc of water}} = \frac{35.944 \text{ g of NaCl}}{100.000 \text{ cc of water}}$	

flask is then evaporated to complete dryness and the exact weight of the flask and dry salt is determined. From this weight, the other data, and the known density of water at 20°C, the solubility is determined as noted in Table 11.1.

The solubilities of the majority of the known substances have been determined in appropriate solvents and are given in handbooks and solubility tables.

The term *miscibility* is commonly used in place of solubility when referring to a solution of a liquid in a liquid. Two liquids are said to be *completely miscible* when a homogeneous solution is formed, no matter in what proportions they are mixed. When there is a limit to the solubility of each in the other they are said to be *partly miscible.* If they are completely insoluble in each other they are said to be *immiscible.* Ordinary alcohol and water are *completely miscible;* ether and water are *partly miscible;* water and mercury are *immiscible.* If equal volumes of ether and water are shaken together in a cylinder and the contents are allowed to stand, two layers will form (see Figure 11.2). The top (lighter) layer is a saturated solution of water in ether, while the bottom

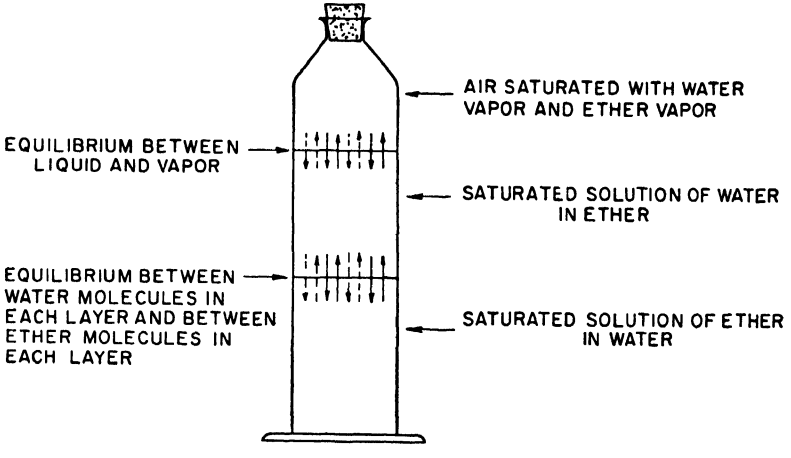


Figure 11.2. Equilibrium in a saturated solution of two partially miscible liquids.

layer is a saturated solution of ether in water. The two saturated solutions are in equilibrium with each other. That means that, at the interface, ether molecules are going from the top layer into the bottom layer and from the bottom layer into the top layer at the same rate. Likewise, water molecules are going from bottom to top at the same rate as they are going from top to bottom.

11.5 Factors that affect the solubility of a solute in a solvent.

1. *Specific character of the solute and the solvent.* The solubilities of different solutes in a specific solute, water for example, vary greatly. Some are highly soluble, meaning thereby that a great many grams of the solute will dissolve in 100 g of water. Others are only moderately soluble, while some are completely insoluble (do not dissolve at all) or are only very slightly soluble. Likewise, the solubility of a specific solute in different solvents may vary greatly. Potassium iodide, for example, is very soluble in water, moderately soluble in liquid NH_3, liquid SO_2, and alcohol, but completely insoluble in ether, benzene, and carbontetrachloride.

The following rules are valuable, but not infallible, in determining the effect of the character of solute and solvent on solubility.

(a) Strongly polar liquids such as H_2O, HF, and molten salts tend to dissolve electrovalent compounds (salts and metal oxides and hydrox-

TABLE 11.2

SOLUBILITY RULES FOR SALTS AND BASES

1. The nitrates, chlorates, and acetates of all metals are soluble in water.

2. All common sodium, potassium, and ammonium salts are soluble in water.

3. The chlorides, bromides, and iodides of all metals except lead, silver, and mercury(I) are soluble in water. The iodides HgI_2, BiI_3, and CuI are insoluble in water. The lead salts $PbCl_2$, $PbBr_2$, and PbI_2 are soluble in hot water. The water-insoluble chlorides, bromides, and iodides are also insoluble in dilute acids.

4. The sulfates of all metals, excepting lead, mercury(I), barium, strontium, and calcium are soluble in water. Silver sulfate is slightly soluble. The water-insoluble sulfates are also insoluble in dilute acids.

5. The carbonates, phosphates, borates, sulfites, chromates, and arsenates of all metals except sodium, potassium, and ammonium, are insoluble in water but soluble in dilute acids. The salt $MgCrO_4$ is soluble in water; $MgSO_3$ is very slightly soluble in water.

6. The sulfides of all metals except barium, strontium, calcium, magnesium, sodium, potassium, and ammonium are insoluble in water.

7. The hydroxides of sodium, potassium, and ammonium are very soluble in water. The hydroxides of calcium, strontium and barium are moderately soluble. The oxides and hydroxides of all other common metals are insoluble.

ides) and polar covalent compounds (HCl, HBr, HI, H_2S, NH_3, SO_2, SO_3, P_4O_{10}, C_2H_5OH, CH_3OH, $C_{12}H_{22}O_{11}$); they do not, however, tend to dissolve nonpolar compounds (CCl_4, CS_2, CH_4, C_6H_6, C_5H_{12}, and other hydrocarbons).

(b) Strongly nonpolar liquids such as CCl_4 (carbon tetrachloride), C_6H_6 (benzene), CS_2 (carbon disulfide), $CHCl_3$ (chloroform), and C_5H_{12} (pentane) tend to dissolve nonpolar or slightly polar compounds, but do not tend to dissolve electrovalent compounds and strongly polar covalent compounds.

The relation between polarity and solubility may be accounted for as follows: A solid crystal will dissolve in a liquid if the mutual force of attraction of molecules of the liquid for molecules of the solid is *greater* than the force of attraction between molecules of the solid; if it is *less*, the solid will not dissolve. The total force of attraction of molecules of a liquid for molecules of a solid is the sum of at least two effects: (1) the surface attraction and gravitational force between two bodies, and (2) the electric force of attraction between dipoles. If the liquid and solid are both strongly dipolar in character, the second force will be large,

TABLE 11.3

SOLUBILITY OF GASEOUS SUBSTANCES

1. Compounds which are gases at ordinary temperatures:

   NH_3, CH_4, HF, HCl, HBr, HI, H_2S, CO_2, SO_2, CO

2. Compounds which decompose at ordinary temperatures to yield gaseous products:

   $H_2CO_3 = H_2O + CO_2$, $H_2SO_3 = H_2O + SO_2$, $NH_4OH = H_2O + NH_3$

3. Solubility of gases in water at 20°C:
   (a) Very soluble in water (400 to 700 volumes of gas per volume of water):

   HCl, HF, HBr, HI, NH_3

   (b) Fairly soluble in water (40 volumes of gas per volume of water):

   SO_2

   (c) Slightly soluble in water (1 to 2.5 volumes of gas per volume of water):

   CO_2, Cl_2, H_2S

   (d) Very slightly soluble in water (1.5 to 3.0 volumes of gas per 100 volumes of water):

   N_2, H_2, CO, O_2, CH_4

and the tendency of the solid to dissolve will be high. A nonpolar liquid molecule will not exert an electric force on a polar solid, and a polar liquid will likewise not exert an electric force on a nonpolar solid.

The tendency of a strongly nonpolar solvent to dissolve a nonpolar solute can be accounted for by the fact that, since molecules of the solute are weakly bound to each other, even the comparatively weak attraction exerted upon them by the solvent molecules is sufficient to pull them into solution. Since the solvent molecules are nonpolar, and hence are not strongly bound together, they are quite free to attract molecules of solute. In contrast, the molecules of a polar solvent are so firmly bound together that they are not free to attract the molecules of a nonpolar solute; as a result the solute is not dissolved even though the molecules of the latter are quite easily pulled into solution. *Solution will occur only when the force of attraction between molecules of solvent and solute is greater than both the attraction of solute molecules for each other and the attraction of solvent molecules for each other.* Solution can result if all three are high, as when a strongly polar liquid dissolves a salt, or if all three are low, as when a nonpolar solvent dissolves a nonpolar solute.

Within the range covered by the above generalizations there is great variation in solubility. Thus, Na_2CO_3, $CuCl_2$, $MgSO_4$, $(NH_4)_3PO_4$, and K_2SO_3 are all highly soluble in water, while $CaCO_3$, AgCl, $BaSO_4$, $Mg_3(PO_4)_2$, and $SrSO_3$ are practically insoluble. The hydroxides KOH and NaOH are highly soluble, $Ca(OH)_2$, $Ba(OH)_2$, and $Sr(OH)_2$ are moderately soluble, while the hydroxides of the other common metals are insoluble. That means that the specific character of the compound has a large bearing on its solubility.

Experimentally determined variations in solubility among salts and bases and among gaseous substances are resolved in the solubility rules given in Tables 11.2 and 11.3.

2. *The temperature.* (a) Increase in temperature generally increases the solubility of a solid in a liquid, and also of a liquid in a liquid. If heat is absorbed when a solute dissolves in its saturated solution, increase in temperature increases the solubility; if heat is given off, the solubility is decreased; most solid and liquid solutes fall in the first category but may fall in the second. The magnitude of the increase varies from one solute to another; it cannot be calculated from any law or formula but must be determined experimentally. The effect of change in temperature on the solubility is commonly represented by plotting the experimentally determined solubility of the solute (usually in grams of solute per 100 g of solvent) as a function of the temperature; the result is a *solubility curve.* A typical collection of experimentally deter-

mined solubility data is given in Table 11.4. The solubility curves drawn from these data are given in Figure 11.3. A relatively flat solubility curve (NaCl) means that there is only a slight change in solubility

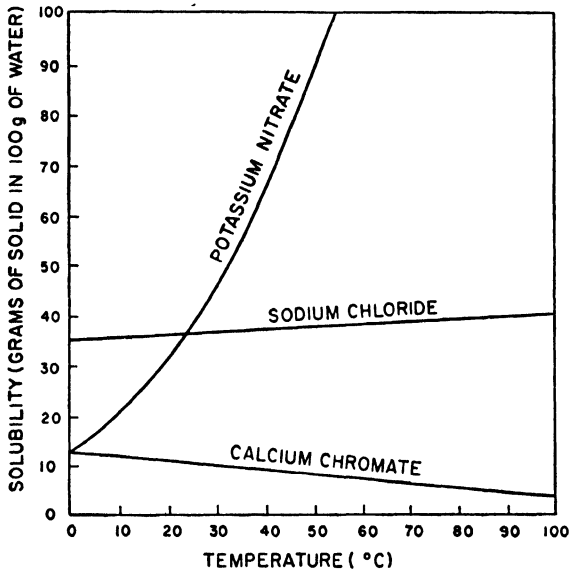


Figure 11.3. Solubility curves.

with change in temperature, whereas a curve that rises sharply (KNO_3) indicates a pronounced temperature effect. The solubility of calcium chromate ($CaCrO_4$) decreases with increase in temperature.

TABLE 11.4

SOLUBILITY TABLE

Temp (°C)	*Calcium chromate*	*Potassium nitrate*	*Common salt*
0	13.0	13.3	35.7
10	12.1	21.1	35.8
20	10.4	31.2	36.0
30	9.4	44.5	36.3
40	8.5	64.0	36.6
50	7.3	86.0	37.0
60	6.1	111.0	37.3
70	5.3	139.0	37.9
80	4.4	171.5	38.4
90	3.8	208	39.1
100	3.2	249	39.8

Once the solubility curve for a compound has been drawn, it can be used to determine the quantity of the compound that will dissolve in

any quantity of water, and the quantity of water required to dissolve any quantity of compound at any temperature within the range covered by the curve. Thus the question, How many grams of KNO_3 will dissolve in 160 g of water at 25°C? can be answered by observing, from the curve, that 100 g of water will dissolve about 38.5 g of KNO_3. By the use of the factor relationship,

$$160 \text{ g of water} \times \frac{38.5 \text{ g of } KNO_3}{100 \text{ g of water}} = 61.5 \text{ g of } KNO_3$$

or the proportion,

$$\frac{38.5 \text{ g of } KNO_3}{100 \text{ g of water}} = \frac{X \text{ g of } KNO_3}{160 \text{ g of water}}$$

we can calculate that 61.5 g of KNO_3 will be dissolved.

(b) *Increase in temperature decreases the solubility of any gas in any liquid.* The decrease in solubility of a gas in a liquid with increase in temperature is well illustrated by what happens to a glass of cold cola or other carbonated drink when it warms up. Carbonated drinks are saturated solutions of CO_2 gas in water, with, of course, some added flavoring and coloring. When the drink warms up, gas bubbles are seen to collect on the inner sides of the glass and escape from the surface. These bubbles are CO_2 gas, and they are escaping because the ability of water to dissolve CO_2 decreases as the temperature increases. The escape from solution of a dissolved gas is called *effervescence;* in this instance the solution *effervesces* because the solubility of CO_2 gas in water is decreased by an increase in temperature.

The bubbles that first appear when cold drinking water is heated are air. Natural water contains dissolved air. When the temperature of the water is increased the solubility of air in the water decreases. As a result, bubbles of air escape. Boiled water contains no dissolved air because the solubility of the gas in water is reduced to zero at the boiling point.

3. *The pressure.* An increase in pressure increases the solubility of a gas in a liquid but has practically no effect on the solubilities of liquids and solids in liquids. The fact that the solubility of a gas in a liquid increases with increase in pressure, and conversely, decreases with decrease in pressure, is well illustrated by the familiar effervescence which takes place when a bottle of pop or other carbonated drink is unstoppered. The CO_2 gas with which the pop is charged is introduced under high pressure. When that pressure is relieved, the solubility of the CO_2 in water decreases and the excess gas which will not stay in solution at the lower pressure escapes and effervescence takes place.

In the case of slightly soluble gases such as H_2, N_2, and O_2 (see

Table 11.3) at constant temperature, *the solubility is directly proportional to the partial pressure of the gas.* Furthermore, in a mixture of such gases *each gas dissolves independently of the other and in proportion to its own partial pressure.* These generalizations are known as *Henry's law;* highly soluble gases do not obey this law.

11.6 Supersaturated solutions. The statement was made in 11.1 that a solution is *saturated* when it has dissolved all the solute that it is capable of holding at a given temperature. One might conclude from this statement that a saturated solution represents the maximum quantity of solute that can ever be present in a given amount of solution at a given temperature. Actually, this is not always the case. To illustrate: If a solution which is saturated with $NaC_2H_3O_2 \cdot 3H_2O$ at 80°C is cooled slowly, *in the complete absence of crystals of the solute,* the temperature can be brought to 20°C or lower and kept there almost indefinitely without any crystallization of solute taking place. This happens in spite of the fact that the solubility of sodium acetate in water decreases sharply when the temperature decreases. Quite obviously, the solution that has been obtained by cooling a saturated solution at 80°C to 20°C contains more solute than it will normally dissolve at 20°C; it is said to be *supersaturated,* and the *degree of supersaturation* is determined by the difference in the amount of solute actually in solution and the amount that can normally be dissolved. Supersaturation is obviously some sort of a metastable condition. Crystals of $NaC_2H_3O_2 \cdot 3H_2O$ should begin to crystallize out just as soon as the temperature falls below 80°C, but for some reason they fail to do so in this case. As a result the solution contains more solute than it would hold if it were in equilibrium with excess solute.

If one tiny crystal of $NaC_2H_3O_2 \cdot 3H_2O$ is added to the supersaturated solution at 20°C, crystallization of solute immediately begins to take place and continues until the "super" or excess solute is crystallized out and a saturated solution remains. Heat is given off during this crystallization process. Not all solutes form supersaturated solutions, but a great many do.

11.7 Heat of solution. When a *solid* is dissolved in a liquid two changes may take place: (1) the crystal structure of the solid is broken down; this requires absorption of heat just as melting the solid absorbs heat (heat of fusion); (2) the molecules or ions of the solute may react with the molecules of the solvent and this may either evolve or absorb heat. The net heat effect is the sum of what happens in (1) and (2). In most instances this net effect is absorption of heat. As a result, *the*

temperature generally falls when a solid is dissolved in a liquid. The overall heat effect is called *heat of solution.*

When a *gas* dissolves in a liquid: (1) the gas changes to the condensed state of a liquid, and this evolves heat just as condensation of a vapor evolves heat (heat of vaporization); (2) the molecules of the dissolved gas may react with molecules of the solvent and this may either evolve or absorb heat. In most instances the net effect of (1) and (2) is evolution of heat. As a result *the temperature generally rises when a gas dissolves in a liquid.*

When a *liquid* dissolves in a liquid there is no change of state corresponding to fusion or vaporization, so there is no evolution or absorption of heat on this account. The small heat of solution that may be observed therefore arises from the reaction between molecules of solute and solvent.

11.8 Concentration of a solution. A solution which contains a small amount of solute in a relatively large amount of solvent is said to be *dilute;* one which contains a large amount of solute in a relatively small amount of solvent is said to be *concentrated.* The terms *dilute* and *concentrated* are descriptive in that they tell us whether a solution contains little solute or much solute, but they do not tell us the exact amount. The term *concentration,* however, refers to the exact amount of solute that is present in an exact amount of solution or an exact amount of solvent.

The terms that are commonly used to denote the concentration of a solution and the units in which concentration is expressed in each are:

1. *Molarity. Molarity of a solution represents the number of moles of solute per liter of solution.* A molar solution of NaCl is designated by the notation 1 *M* NaCl; it contains 1 mole (58.5 g) of NaCl in a liter of solution. The notation 0.2 *M* K_2SO_4 refers to a 0.2 molar solution of K_2SO_4; it contains 0.2 mole (34.85 g) of K_2SO_4 in a liter of solution. The notation 12 *M* HCl refers to a solution whose *concentration* is 12 moles of HCl per liter of solution. A solution prepared by dissolving 53 g (0.5 mole) of Na_2CO_3 in enough water to give a liter of solution would be 0.5 *M* Na_2CO_3.

Expressed in mathematical form,

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

For a solution prepared by dissolving 15 moles of HNO_3 in enough water to yield 12 liters of solution,

$$\text{molarity} = \frac{15 \text{ moles of } HNO_3}{12 \text{ liters of solution}} = 1.25\ M$$

Likewise for a solution obtained by dissolving 14.92 g (0.2 mole) of KCl in enough water to give 400 ml of solution,

$$\text{molarity} = \frac{0.2 \text{ moles}}{0.4 \text{ liters}} = 0.5\ M$$

2. *Per cent strength.* Per cent means parts per 100 parts. Therefore *per cent strength of a solution means parts by weight of solute per 100 parts by weight of solution.* A solution prepared by dissolving 10 g of NaCl in 90 g of water to give 100 g of solution would be a 10% solution. A 25% solution of KCl in water would contain KCl and solution in the ratio of 25 parts by weight of KCl to 100 parts by weight of solution.

Since a ratio can always be expressed in the form of a fraction, we can express the concentration of the solution formed by dissolving 25 g (parts by weight) of KCl in enough water to give 100 g of solution by the fraction

$$\frac{25 \text{ g of KCl}}{100 \text{ g of solution}}$$

This fraction, like all fractions, when solved will give an answer which represents "parts per 1"; in this case "grams of KCl per 1 gram of solution." To convert this answer to parts per 100 we will multiply by 100. We can therefore express the concentration of a solution in units of per cent strength by the formula

$$\text{per cent strength} = \frac{\text{grams of solute}}{\text{grams of solution}} \times 100\%$$

Since the weight of the solution is the sum of the weights of the solute and solvent, a more general form of the expression would be

$$\text{per cent strength} = \frac{\text{grams of solute}}{\text{grams of solute} + \text{grams of solvent}} \times 100\%$$

We can of course use any unit of mass (milligrams, kilograms, pounds, tons) as long as both solute and solvent are expressed in the same unit.

It is important to note that units of mass, not units of volume, are used in expressing per cent strength. Ten grams of NaCl dissolved in enough water to give 100 cc of solution would not be a 10% solution unless the density of the solution was exactly 1 g/cc. If the density of the solution was, let us say, 1.12 g/cc, the weight of the 100 cc of solution would then be 112 g. The per cent strength would then be

$$\frac{10 \text{ g of NaCl}}{112 \text{ g of solution}} \times 100\% = 8.93\%$$

3. *Molality. Molality of a solution represents the number of moles of solute per 1000 g of solvent.* It should be noted, at the outset, that, whereas the terms *molarity* and *molality* sound alike they refer to two somewhat different concepts; *molarity* means moles of solute per *liter* of *solution,* while *molality* refers to moles of solute per *1000 g* of *solvent.* A solution prepared by dissolving 58.5 g (1 mole) of NaCl in 1000 g of water is *1 molal;* a solution prepared by dissolving 117 g (2 moles) of NaCl in 2000 g of water is likewise *1 molal.* A solution prepared by dissolving $\frac{1}{4}$ mole of NaCl in 250 g of water has the same concentration as the two just described and is therefore *1 molal.* We can accordingly express molality by the formula

$$\text{molality} = \frac{\text{moles of solute}}{1000 \text{ g of solvent}}$$

4. *Normality.* The discussion of this method of expressing concentration will be given in Chapter 13.

5. Some authors refer to the *formality* of a solution, and mean thereby the concentration in *gram-formula weights* of solute per liter of solution. Formality is therefore synonymous with molarity.

11.9 Separation of a solute from a solvent. A solute may be separated from a solvent or recovered from a solution in the following ways.

1. *By evaporation.* The volatile solvent is boiled off into the atmosphere or under a hood; the nonvolatile, solid solute remains behind as a residue. This is widely used in the laboratory and in industry when water is the solvent and its recovery is unnecessary. If recovery of the solvent is necessary the evaporation is carried out in a distillation flask and the vapors are condensed (see Figure 2.6).

2. *Concentration of the solution by evaporation, followed by cooling and crystallization of the solid solute.* This method is widely used in the commercial manufacture of salts and other compounds, cane sugar for example. Well-defined crystals are formed as a product. By properly controlling the evaporation and cooling, separation of the component solutes in a complex solution can be accomplished.

3. *By fractional distillation.* This method is widely used in the laboratory and in industry for separating and recovering the liquid components of a solution of one or more liquids in another liquid. It depends for its operation on the fact that when a mixture of two or more liquids is distilled, the vapors that come off when the solution first

begins to boil contain a higher per cent of the lower boiling component than does the liquid from which these vapors are escaping. The liquid "fraction" obtained by condensing these vapors is therefore richer in the lower-boiling (more volatile) component. As the distillation proceeds, the liquid that remains in the flask contains a smaller per cent of the more volatile component and a higher per cent of the higher-boiling (less volatile) component. At the same time, the boiling point of the solution rises, and the successive "fractions" contain a decreasing per cent of the lower boiling (more volatile) component, and an increasing per cent of the higher boiling component. If the successive fractions are redistilled and refractionated one can effect an almost complete separation of the solution into its liquid components. The refractionations are accomplished in one continuous operation by using a tall fractionating column (see Figure 11.4).

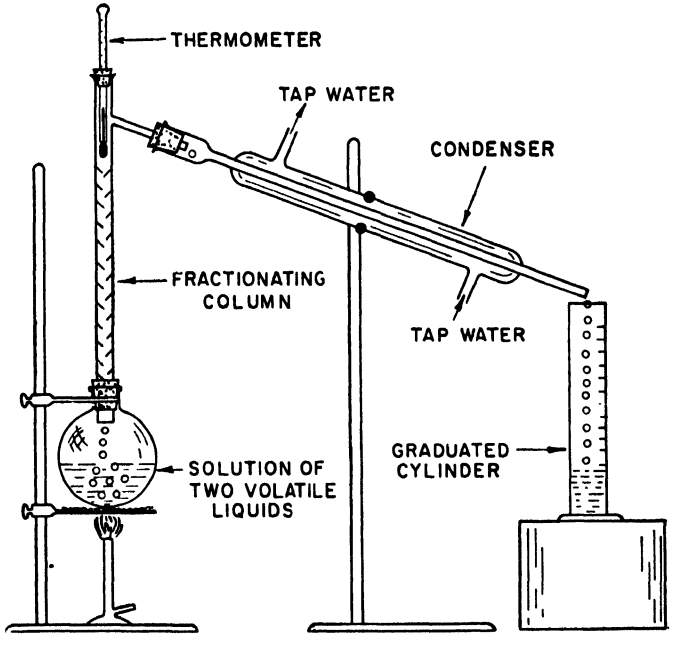


Figure 11.4. Use of a fractionating column in fractional distillation of two volatile liquids.

4. *By extraction with a new liquid solvent* in which the solute is very soluble but the solvent is insoluble or very slightly soluble. Thus iodine can be extracted from water solution by shaking with carbon tetrachloride. Iodine is very soluble in CCl_4, while water is almost completely insoluble. The solution of iodine in CCl_4 settles to the bottom of the

extraction chamber and can be drawn off. The volatile CCl_4 is then distilled off and recovered, leaving the iodine as a solid residue. The extraction process is widely used in industry for the recovery of solutes.

Questions and Problems

1. Define and illustrate each of the following: solution; solvent; solute; homogeneous; component; solubility; concentration; dilute solution; concentrated solution; saturated solution; unsaturated solution; supersaturated solution; per cent strength; molarity; molality; formality; miscibility; immiscible; solubility curve; effervescence; polar liquid; distillation; evaporation; fractional distillation; extraction.

2. Point out the exact kinetic process that is believed to take place when a solid such as sugar dissolves in water to form a saturated solution.

3. Point out the exact meaning of the expression "a saturated solution is in equilibrium with excess solute."

4. A small depression was gouged out of a crystal of pure $C_{12}H_{22}O_{11}$ (sugar), which was then dropped into a saturated solution of sugar in water. On examining the crystal a few days later, the depression had disappeared and a perfect crystal had formed. The weight of this perfect crystal was exactly the same as that of the original imperfect one. Explain.

5. How would you determine, experimentally, whether a given solution is unsaturated, saturated, or supersaturated?

6. Account for the evolution of heat when excess solute crystallizes from a supersaturated solution.

7. How would you prepare a saturated solution of a salt in water? A supersaturated solution? An unsaturated solution?

8. How would you recover pure sugar from a mixture of sugar and sand?

9. How would you determine the solubility of KCl in water at 20°C? Of oxygen gas in water at 25°C? Of ether in water at 20°C?

10. Most artesian (spring) water is observed to effervesce when it flows out into the air. Account for this effervescence.

11. Account for the following behavior: When a beaker of cold tap water is heated with the object of producing boiling, the following is observed to happen: Small bubbles first form; these bubbles tend to stick to the walls of the beaker. As heating continues these bubbles are dislodged and escape. Later, larger bubbles begin to form at the bottom of the beaker. Soon the water boils vigorously.

12. Why does a carbonated drink "fizz" when poured into a glass? Why does an iced drink fizz less than a warmer one?

13. The following procedure is recommended for growing large crystals of a solid: Place one or two small crystals of the solid in its saturated solution contained in an open flask. Allow to stand for several weeks, keeping the temperature constant meanwhile. Explain why this yields large crystals.

14. Why are water and liquid hydrogen fluoride excellent solvents for salts but poor solvents for such substances as paraffin wax, benzene, carbon tetrachloride, and gasoline?

15. Why are benzene (C_6H_6) and heptane (C_7H_{16}) excellent solvents for waxes, greases, fats, and oils but poor solvents for salts?

16. Account for the fact that the temperature of a solution formed by dissolving a solid in a liquid in an open beaker is usually lower, immediately following solution, than the temperature of the original solid and liquid, while the temperature of a solution formed by dissolving a gas in a liquid is usually higher than the temperature of the original gas and liquid.

17. How is the solubility of a gas in a liquid affected by (a) an increase in temperature; (b) an increase in pressure?

18. State Henry's law relating to the solubility of a gas in a liquid.

19. How does an increase in temperature effect the solubility of a solid in a liquid? Of a liquid in a liquid?

20. How would you prepare a liter of a 0.2 *M* solution of KBr in water?

21. How would you prepare 400 ml of 0.4 *M* $NaNO_3$?

22. How would you prepare 80 g of a 15% solution of sugar in water?

23. How many grams of C_2H_5OH must be dissolved in 400 g of water to give a 0.5 molal solution?

24. Sixty grams of a 12% solution of NaCl in water were evaporated to dryness. How many grams of dry NaCl were obtained?

25. How many grams of water and how many grams of salt would you have to mix in order to get 48 g of an 8% solution?

26. How many grams of KOH will be required for preparation of 1500 ml of 0.12 *M* KOH?

27. How many grams of NaCl are there in 400 ml of 0.4 *M* NaCl?

28. A 15% solution of salt in water has a density of 1.2 g/cc. Twenty cubic centimeters of this 15% salt solution were evaporated to dryness. How many grams of dry salt were obtained?

29. A solution contained 12 g of NaCl in 750 ml of solution. Calculate its molarity.

30. Calculate the molarity of a 20% solution of NaCl whose density is 1.2 g/cc.

31. Ten cubic centimeters of a 70% solution of sulfuric acid of density 1.61 g/cc were dissolved in enough water to give 25 cc of solution. Calculate the molarity of the final solution.

32. Calculate the density of 3.58 *M* H_2SO_4, which contains 29.0% H_2SO_4.

33. Eighteen liters of dry HCl gas measured at 20°C and 740 mm are dissolved in enough water to give 400 ml of solution. Calculate the molarity of the solution.

34. How many molecules of sugar ($C_{12}H_{22}O_{11}$) are there in 200 ml of a 1.20 *M* solution?

35. Calculate the volume of hydrochloric acid of density 1.12 g/cc and containing 40% by weight of HCl required to liberate 200 cc of dry hydrogen gas when mixed with excess Mg at 0°C and 760 mm.

36. A volume of 130 ml of hydrochloric acid was treated with an excess of zinc. A total of 7.13 l of dry hydrogen gas measured at 220°C and 738 mm was liberated. Calculate the molarity of the acid.

37. An excess of Mg was added to 200 g of a 0.4 molal solution of H_2SO_4 in water. How many liters of hydrogen gas, collected and measured over water at 22°C and 746 mm, were obtained?

CHAPTER 12

Nonelectrolytes and Electrolytes

12.1 Influence of a solute on the freezing point and boiling point of a solvent. Nonelectrolytes. Electrolytes. If 1 mole (342 g) of sugar ($C_{12}H_{22}O_{11}$) is dissolved in 1000 g of water, the resulting solution freezes at -1.86°C and boils at 100.52°C at a pressure of 760 mm. Since the freezing point of water is 0°C and the boiling point is 100°C, the 1 mole of solute has depressed the freezing point of 1000 g of water 1.86°C and raised the boiling point 0.52°C. A great many other solutes show exactly the same behavior as does sugar, that is, 1 mole of solute dissolved in 1000 g of water raises the boiling point 0.52°C and lowers the freezing point 1.86°C. Among these solutes are dextrose ($C_6H_{12}O_6$), glycerol ($C_3H_5(OH)_3$), urea ($CO(NH_2)_2$), and ethylene glycol ($C_2H_4(OH)_2$).

In addition to the fact that they all have the same constant effect on the freezing point and boiling point of water, these solutes all have one other property in common; *their water solutions do not conduct an electric current.*

If 1 mole of any acid (a nonvolatile one), base, or salt is dissolved in 1000 g of water, the freezing point is in every case depressed more than 1.86°C, and the boiling point is in every instance raised more than 0.52°C. In addition to this abnormally large effect on the freezing point and boiling point of water, these solutes all have one other property in common; *their water solutions all conduct the electric current.*

We can summarize these facts by stating that

1. *Solutes whose water solutions do not conduct electricity generally show a normal effect on the boiling point and freezing point of water;* 1 mole of such a solute dissolved in 1000 g of water raises the boiling point 0.52°C and lowers the freezing point 1.86°C.

2. *Solutes whose water solutions conduct electricity show an abnormal effect on the boiling point and freezing point of water;* 1 mole of such a solute dissolved in 1000 g of water raises the boiling point *more* than 0.52°C and lowers the freezing point *more* than 1.86°C.

We may conclude from these observations that the factor or property which causes the one group of solutes to have abnormal boiling point and freezing point effects is probably the same property that causes

their solutions to be conductors of electricity. The question is, What is this property?

Before answering this question we should first answer the question, Why do nonconductors all have the same molal effect on the freezing point and boiling point? We should note, first, that the true chemical formula for each of these solutes is known. That means that 1 mole (1 gram-molecular weight) of each will contain 6.023×10^{23} molecules. One can conclude, therefore, that the reason why 1 mole of $C_{12}H_{22}O_{11}$, $C_6H_{12}O_5$, $C_3H_5(OH)_3$, $CO(NH_2)_2$, and $C_2H_4(OH)_2$ will each depress the freezing point the same amount, 1.86°C, is that each contains 6.023×10^{23} molecules. It follows, from this conclusion, that the effect of a solute on the freezing point and boiling point of a solute is determined only by the number of individual particles in solution and is not effected by the weight or chemical composition of the particle.

These deductions lead to the conclusion that the solutes which have an abnormal boiling point and freezing point effect must yield more than 6.023×10^{23} particles per mole when they dissolve in water, and that the ability of the solution to conduct electricity is the direct result of the presence of these extra particles. If a solution conducts electricity it is logical to assume that it contains electrically charged atoms or groups of atoms; such charged atoms or groups of atoms, called ions, have already been encountered in Chapter 7. Therefore we can conclude that ions are set free in solution when acids, bases and salts are dissolved in water. Since the solution as a whole is neutral, the number of positive ion charges must be equal the number of negative charges.

Those substances whose water solutions conduct electricity, and hence are concluded to contain positive and negative solute ions, are called *electrolytes*. Substances whose water solutions do not conduct electricity, and hence are concluded to yield no ions, are called *nonelectrolytes*. We can then state that *1 mole of a nonelectrolyte when dissolved in 1000 g of water will lower the freezing point 1.86°C and raise the boiling point 0.52°C*. The values 1.86 and 0.52 are referred to as the *freezing point constant* and the *boiling point constant*, respectively, for water.

12.2 When and how are ions formed? The answer to this question depends on whether the electrolyte is an electrovalent compound or a covalent compound.

1. *Electrovalent compounds.* Experiments show that *all soluble electrovalent compounds are electrolytes.* As was pointed out in Chapter 7, electrovalent compounds are formed by *transfer* of electrons; in the process positive and negative ions are produced. The resulting solid

compounds (salts and metal oxides and hydroxides) all have an ionic crystal lattice. That means that, in the case of these electrovalent compounds, the ions are formed when the compound is formed; they exist before the compound is dissolved in water. When such a compound is dissolved the ionic crystal lattice is broken down and the ions are thereby set free in solution; the water merely acts as a solvent. Typical equations to illustrate the setting free of these already-existing ions are:

(1) $K^+Cl^- = K^+ + Cl^-$

(2) $Na^+Br^- = Na^+ + Br^-$

Since it is understood that all salts and metal oxides and hydroxides have an ionic crystal lattice it is customary to omit the charges when writing the formula of one of these compounds. The equations depicting the setting free of the ions then become:

(3) $NaCl = Na^+ + Cl^-$

(4) $K_2SO_4 = 2\,K^+ + SO_4^{--}$

(5) $LiNO_3 = Li^+ + NO_3^-$

(6) $BaBr_2 = Ba^{++} + 2\,Br^-$

(7) $Ca(OH)_2 = Ca^{++} + 2\,OH^-$

(8) $Na_3PO_4 = 3\,Na^+ + PO_4^{---}$

(9) $Al_2(SO_4)_3 = 2\,Al^{+++} + 3\,SO_4^{--}$

2. *Covalent compounds.* Some covalent compounds are electrolytes; most of them, however, are nonelectrolytes. Covalent compounds are formed originally from the constituent elements by the *sharing* of pairs of electrons; no ions are produced in the process and the solid compound does not have an ionic crystal lattice. This means that a covalent electrolyte (a covalent compound which, when dissolved in water, yields ions and produces a conducting solution) is not ionized until it is dissolved in water. It seems logical therefore to conclude that the water plays an active role in the ionization process. It is believed that the molecules of water and covalent electrolyte are attracted to each other and become bound together by a coordinate-type bond. This binding causes some shift in the relative positions of the electrons in the water molecule and also in the solute molecule. As a result of this shift a weak bond is created, and this bond breaks. In the breaking process the more electropositive part of the ruptured molecule gives up one or more electrons to form a positive ion, while the more electronegative part retains these electrons and becomes a negative ion. If the water molecules and covalent solute molecules are not strongly attracted to each other or, more likely, if their attachment to each other does not

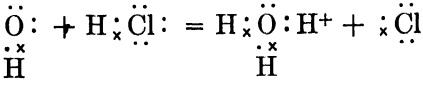
produce weak bonds, there will be no breakage of bonds, and no ions will be formed. In this case the covalent compound is a *nonelectrolyte.*

The following equation is postulated to represent the ionization of a typical covalent compound:

(10) $$H_2O + HCl = H_2O{\cdot}H^+ + Cl^-$$

The exact formula of the hydrated hydrogen ion is open to question; it may well be $(H_2O)_2{\cdot}H^+$ rather than $H_2O{\cdot}H^+$. Assuming that it is $H_2O{\cdot}H^+$, the detailed electronic picture of the ionization process may be represented as follows (see also Figures 7.11 and 7.13).

(11)



Note that the H from HCl coordinates with the O in H_2O. At the same time the bond between H and Cl is broken. The Cl, being more electronegative than H, retains the hydrogen electron and becomes the Cl^- ion. This leaves an hydrogen ion attached to the H_2O molecule.

This same type of reaction occurs when *any acid* is dissolved in water.

(12) $$H_2O + HBr = H_2O{\cdot}H^+ + Br^-$$

The $H_2O{\cdot}H^+$ ion is referred to as a hydrated *hydrogen ion,* a hydrated *proton,* or a *hydronium ion.* Its formula may be represented as H_3O^+. It is common practice to ignore the H_2O when representing the formula of the hydrated hydrogen ion (hydronium ion) and refer to it simply as a hydrogen ion with the formula H^+. In line with this practice the ionization that takes place when any acid, such as HCl, HBr, HI, H_2S, H_2SO_4, and H_3PO_4 is dissolved in water to form a very dilute solution is

(13) $$HI = H^+ + I^-$$

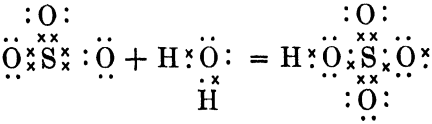
(14) $$H_2S = 2\,H^+ + S^{--}$$

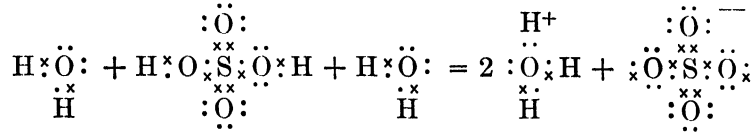
(15) $$H_2SO_4 = 2\,H^+ + SO_4^{--}$$

(16) $$H_3PO_4 = 3\,H^+ + PO_4^{---}$$

When the *oxide of a nonmetal,* such as SO_3, is dissolved in water to form an acid, one can visualize a two-step reaction taking place:

(17)



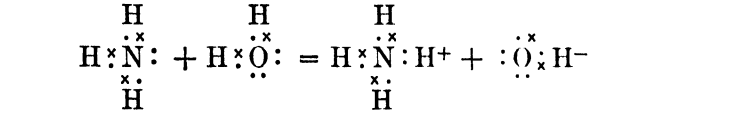
(18) 

Presented in nonstructural form, reactions (17) and (18) would be

(19) $$SO_3 + H_2O = H_2SO_4$$

(20) $$H_2SO_4 + 2\,H_2O = 2\,H_2O{\cdot}H^+ + SO_4^{--}$$

When ammonia (NH_3) is dissolved in water, the following reaction takes place:

(21) 

This reaction can be represented, more simply, as

(22) $$NH_3 + H_2O = NH_4^+ + OH^-$$

In some instances the reaction that takes place when a covalent electrolyte is ionized is obviously quite involved. Thus when PCl_3 is dissolved in water, PO_3^{---}, Cl^-, and H^+ ions are formed. The over-all equation is

(23) $$PCl_3 + 3\,H_2O = 6\,H^+ + 3\,Cl^- + PO_3^{---}$$

12.3 Character and identity of ions. Cations and anions. Gram-ions. Table 12.1 lists the ions that are formed when different classes of electrolytes are dissolved in water to form very dilute solutions. An examination of this table and the equations (1)–(23) in Section 12.2 leads to the following conclusions about the character and identity of the ions:

1. All acids yield H^+ ions.
2. All bases yield OH^- ions.
3. A binary acid yields a nonmetal negative ion.
4. A ternary acid yields a radical-type negative ion.
5. Bases yield positive metal ions; NH_3 forms the NH_4^+ (ammonium) ion.
6. Every salt yields a positive metal ion and a negative nonmetal or nonmetal-radical ion. In other words, salts yield the positive ions of a base and the negative ions of an acid.

7. Electropositive elements (metals) yield positive ions, while electronegative elements (nonmetals) yield negative ions.

8. Binary nonmetal compounds yield the characteristic ions of an acid (H^+ and nonmetal or nonmetal-radical).

9. Positive ions are called *cations* because they migrate toward the negative pole (*cathode*) during electrolysis. Negative ions are called *anions* because they migrate toward the positive pole (*anode*) during electrolysis.

10. The magnitude of the charge on an ion is the same as the magnitude of the valence of the element or radical that constitutes the ion. For this reason *valence is commonly defined as the charge on an ion.*

11. The sum of the positive charges on the positive ions formed by a mole of electrolyte is equal to the sum of the negative charges on the negative ions.

We shall learn later on that ions of varying degrees of complexity may be present in more concentrated solutions of electrolytes.

Just as the formula of a molecule of an element or compound refers to 1 mole of the substance, so the formula for an ion refers to 1 mole of the ion. A mole of an ion is commonly referred to by the term *gram-ion.* One gram-ion of Na^+ ions is 23 g, while 1 gram-ion of SO_4^{--} is 96 g.

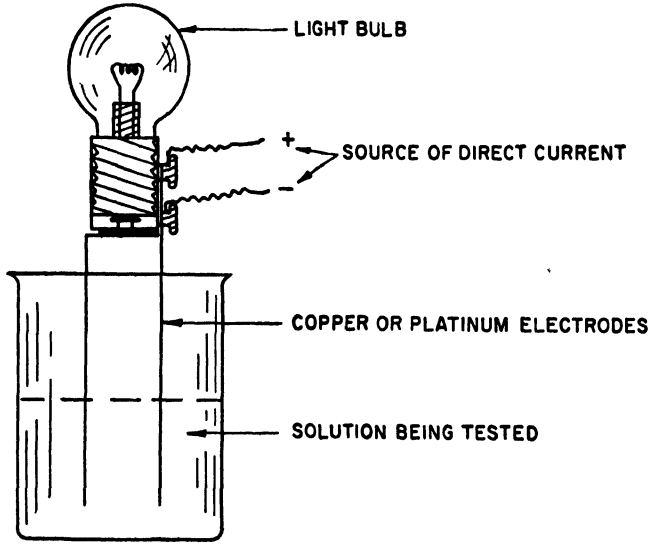


Figure 12.1. Conductivity cell for testing the electrical conductivity of solutions of electrolytes. The better the conductivity the larger the amount of current that will flow and the more brightly the bulb will shine. The better the conductivity of a solution of an electrolyte the stronger the electrolyte.

12.4 Strong electrolytes and weak electrolytes. Exact experimental measurements indicate that solutions of different electrolytes show marked differences in electric conductivity (see Figure 12.1 and Table 12.1). Some are excellent conductors and some are very poor, and between these two extremes are all degrees of conductivity. Since the ability of a solution to conduct electricity is dependent upon the presence of ions, we can conclude that the solutions that are excellent conductors contain a high concentration of ions, while the poor conductors contain relatively low concentrations. To account for the fact that a 1 *M* solution of HCl is an excellent conductor, while a 1 *M* solution of $HC_2H_3O_2$ is a poor conductor, it is postulated that all the molecules of HCl are ionized, while only a small per cent of the $HC_2H_3O_2$ molecules are ionized. Thus 1 *M* NaOH is an excellent conductor, while 1 *M* NH_4OH is a poor conductor; in line with what has just been said about HCl and $HC_2H_3O_2$, 1 *M* NaOH is completely ionized, while 1 *M* NH_4OH is only sparingly ionized.

Electrolytes that are completely ionized are called *strong electrolytes;* those that are not completely ionized are called *weak electrolytes.*

An examination of experimental data of the sort given in Table 12.1 leads to the following conclusions:

1. With very few exceptions all salts are strong electrolytes. (The exceptions that will be encountered in this book are $Pb(C_2H_3O_2)_2$, $HgCl_2$, $CdCl_2$, and $AlCl_3$.)

2. The hydroxides of all group IA and IIA metals except Be and Mg are strong electrolytes and are accordingly classed as *strong bases.* The hydroxides of all other metals (Be and Mg included) are so sparingly soluble in water that even though they are as a rule completely ionized, their solutions contain such low concentrations of ions that for all practical purposes they behave like weak electrolytes; these hydroxides are accordingly classed as *weak bases.*

3. The acids HCl, HBr, HI, H_2SO_4, HNO_3, and $HClO_3$ are strong electrolytes and are accordingly classed as *strong acids;* all other acids that will be encountered in this book are very weak or moderately weak electrolytes and are classed as *weak acids.*

4. A solution of NH_3 in water, commonly referred to as ammonium hydroxide and represented by the formula NH_4OH, is a weak electrolyte, and hence a weak base.

12.5 Determination of the per cent ionization of a weak electrolyte. The per cent ionization of a weak electrolyte can be determined, experimentally, by measuring:

1. *The electric conductivity of a solution of known concentration* (see

TABLE 12.1

IONS FORMED IN DILUTE SOLUTIONS OF VARIOUS ELECTROLYTES

Formula of electrolyte	Class of electrolyte	Type of structure	Ions formed per "molecule" of solute: Cations	Ions formed per "molecule" of solute: Anions	Conductivity of solutions
NaI	Salts	Electrovalent	Na^+	I^-	Excellent
$BaBr_2$			Ba^{++}	$2\ Br^-$	
$CrCl_3$			Cr^{+++}	$3\ Cl^-$	
K_2S			$2\ K^+$	S^{--}	
$Cu(NO_3)_2$			Cu^{++}	$2\ NO_3^-$	
$MnSO_4$			Mn^{++}	SO_4^{--}	
Na_3PO_4			$3\ Na^+$	PO_4^{---}	
K_2CO_3			$2\ K^+$	CO_3^{--}	
$(NH_4)_2SO_3$			$2\ NH_4^+$	SO_3^{--}	
$Cr_2(SO_4)_3$			$2\ Cr^{+++}$	$3\ SO_4^{--}$	
$Mg(ClO_3)_2$			Mg^{++}	$2\ ClO_3^-$	
KOH	Bases (Metal hydroxides)	Electrovalent	K^+	OH^-	Excellent
NaOH			Na^+	OH^-	
$Ca(OH)_2$			Ca^{++}	$2\ OH^-$	
$Ba(OH)_2$			Ba^{++}	$2\ OH^-$	
CsOH			Cs^+	OH^-	
NH_3	Base	Covalent	NH_4^+	OH^-	Poor
HCl	Acids	Covalent	H^+	Cl^-	Excellent
HBr			H^+	Br^-	
HI			H^+	I^-	
H_2SO_4			$2\ H^+$	SO_4^{--}	
HNO_3			H^+	NO_3^-	
$HClO_3$			H^+	ClO_3^-	
HF			H^+	F^-	Poor
$HC_2H_3O_2$			H^+	$C_2H_3O_2^-$	
H_2S			$2\ H^+$	S^{--}	
HCN			H^+	CN^-	
H_2CO_3			$2\ H^+$	CO_3^{--}	
H_3BO_3			$3\ H^+$	BO_3^{---}	
H_3PO_4			$3\ H^+$	PO_4^{---}	
H_3AsO_4			$3\ H^+$	AsO_4^{---}	
H_2SO_3			$2\ H^+$	SO_3^{--}	Moderately good
PBr_3	Binary nonmetal compounds	Covalent	$6\ H^+$	$3\ Br^-$, PO_3^{---}	Excellent
$AsCl_5$			$8\ H^+$	$5\ Cl^-$, AsO_4^{---}	Excellent
SO_2			$2\ H^+$	SO_3^{--}	Moderately good

Figure 12.1). The greater the number of ions that are present in a given volume of solution the better will be its conductivity. The number of ions that form when 1 mole of an electrolyte is dissolved in enough water to give 1 l of solution will obviously depend upon the per cent of the molecules that ionize. Thus, suppose 1 mole (6.023×10^{23} molecules) of some electrolyte, HX, is 100% ionized. Since 1 molecule of HX yields 1 H^+ ion and 1 X^- ion, a total of $2 \times 6.023 \times 10^{23}$ ions will be formed. These $2 \times 6.023 \times 10^{23}$ ions will represent the total number of solute particles in the solution. If only 50% of the HX molecules ionized, the solution would then contain $\frac{1}{2} \times 6.023 \times 10^{23}$ H^+ ions, $\frac{1}{2} \times 6.023 \times 10^{23}$ X^- ions, and $\frac{1}{2} \times 6.023 \times 10^{23}$ un-ionized HX molecules; the total number of ions in this solution would be 6.023×10^{23}, and the total number of solute particles (ions plus un-ionized molecules) would be $1.5 \times 6.023 \times 10^{23}$. Since the conductivity of a system is determined by the number of ions present, the conductivity of a 100% ionized solution of HX would be about twice as great as that of one which was only 50% ionized, four times as great as one which was only 25% ionized, and ten times as great as one which was only 10% ionized. (Because of attraction of ions for each other and for the solvent, the conductivity is not exactly directly proportional to the concentration of ions.) Reversing the procedure, we can measure the electric conductivity, and calculate from this conductivity the per cent ionization of the electrolyte. This method is extremely sensitive and gives very exact results.

2. *The freezing point or boiling point of a solution of known concentration.* The extent to which the freezing point of 1000 g of water is depressed by a solute is, we have learned, directly proportional to the number of solute particles present. Thus if the weak acid HY is not ionized at all, 1 mole dissolved in 1000 g of water would yield 6.023×10^{23} molecules; this 1 mole would depress the freezing point 1.86°C. If the HY is 100% ionized, the 6.023×10^{23} molecules would yield $2 \times 6.023 \times 10^{23}$ particles. This is equivalent to saying that 1 mole of HY yields 2 moles of particles. Half of the particles would be H^+ ions and half of them Y^- ions. Since the freezing point depression depends only upon the number of particles and not on their identity, the $2 \times 6.023 \times 10^{23}$ particles will depress the freezing point 2×1.86°C, or 3.72°C. If the HY is 50% ionized, the solution will contain $\frac{1}{2} \times 6.023 \times 10^{23}$ H^+ ions, $\frac{1}{2} \times 6.023 \times 10^{23}$ Y^- ions, and $\frac{1}{2} \times 6.023 \times 10^{23}$ HY molecules. The total number of particles will be $1.5 \times 6.023 \times 10^{23}$. This is equivalent to saying that there are 1.5 moles of particles present. This number of particles will depress the freezing point 1.5×1.86°, or 2.79°. If the HY is 10% ionized, the solution will contain $0.1 \times 6.023 \times 10^{23}$ H^+ ions,

$0.1 \times 6.023 \times 10^{23}$ Y^- ions, and $0.9 \times 6.023 \times 10^{23}$ HY molecules. The total number of particles will be $1.1 \times 6.023 \times 10^{23}$. That means that there will be 1.1 moles of particles present, and the freezing point will be depressed $1.1 \times 1.86°$ or 2.05°. The same reasoning would apply to the boiling point increase, where the constant is 0.52°. Reversing the procedure, we can therefore measure the freezing point depression or boiling point increase and calculate the per cent ionization. Because the abnormal effect of electrolytes is due to some extent to factors other than the actual number of ions present (attraction of ions for each other and for solvent molecules, for instance), the calculated per cent will not be exact unless exact correction is made for these factors.

The following example will illustrate how a calculation is carried out.

A solution formed by dissolving 1 mole of HZ in 1000 g of water froze at −1.96°C. What is the per cent ionization of the HZ?

Suppose we let X = the fraction of 1 mole of HZ that is ionized. From the ionization equation

$$HZ = H^+ + Z^-$$

we can see that, since 1 mole of HZ yields 1 mole (1 gram-ion) of H^+ and 1 mole (1 gram-ion) of Z^-, the X moles of HZ that ionize will yield X moles of H^+ and X moles of Z^-. Furthermore, since we started with 1 mole of HZ, and X of them ionize, there will remain in solution $1 - X$ moles of un-ionized HZ. The total number of moles (HZ, H^+, and Z^-) in the solution will therefore be $(1 - X) + X + X$ or $1 + X$. These $1 + X$ moles are responsible for the abnormal depression of 1.96°C. Since 1 mole will depress the freezing point 1.86°C, we can set up the proportion

$$\frac{1}{1.86} = \frac{1 + X}{1.96}$$

Solving, we find that

$$X = 0.05$$

The per cent ionization is therefore 5%.

Since a strong electrolyte is presumed to be completely ionized, a 0.1 molal solution of NaCl in water would be expected to freeze at −0.372°C; because it yields 2 gram-ions per mole, the depression should be twice as great as that produced by a nonelectrolyte in a solution of equal molality. The observed freezing point is actually only −0.342°C. If the per cent ionization of the NaCl is calculated in the manner outlined above, using the 0.342° depression, a value of 84% is obtained. All strong electrolytes show similar behavior; the freezing point effect and boiling point effect as well as the electric conductivity are in each instance less than what would be expected if the electrolyte were com-

pletely ionized. The early theory, proposed by the Swedish chemist Arrhenius in 1887, accounted for this behavior by postulating that all electrolytes, strong as well as weak, are incompletely ionized except in infinitely dilute solution; the weaker the electrolyte the lower the per cent ionization. The modern theory, as originally proposed by Debye and Hückel in 1923, postulates that all strong electrolytes are 100 per cent ionized; the anomalous behavior noted above is due to the attraction between the oppositely charged ions in the solution. As a result of this attraction, the individual ions are not completely free to act as independent particles. This causes their conductivity and freezing point and boiling point effect to be less than it would be if each ion were unaffected by the presence of the other ions. The more dilute the solution, the more widely dispersed the ions, the less their influence on each other, and the more nearly ideal their behavior. The modern theory is in line with the concept that electrovalent compounds are formed by transfer of electrons, and hence are completely ionized even before they are put into solution.

It should be noted that the mobility of an ion may be modified by other factors, as for example, association with molecules of the solvent to form *hydrated* or *solvated complex ions* such as $Al(H_2O)_6^{+++}$, or with other ions or reacting molecules to form complex ions of the type HgI_4^{--} and $Cu(NH_3)_4^{++}$.

12.6 Reactions of electrolytes in solution. Not only do solutions of electrolytes contain ions but these ions are believed to be the actual reactants in reactions in which the electrolytes are involved. It was pointed out in Chapter 4 that hydrogen gas can be prepared by reaction of an active metal with a dilute acid. The following equations represent typical reactions:

(1) $Mg + 2\,HCl = MgCl_2 + H_2$

(2) $Zn + H_2SO_4 = ZnSO_4 + H_2$

(3) $2\,Al + 6\,HCl = 2\,AlCl_3 + 3\,H_2$

In the light of what has been presented in this chapter, dilute solutions of the strong acids HCl and H_2SO_4 are in reality solutions of H^+ and Cl^-, and H^+ and SO_4^{--} ions, respectively. Solutions of $MgCl_2$, $ZnSO_4$, and $AlCl_3$ are solutions of Mg^{++} and Cl^-, Zn^{++} and SO_4^{--}, and Al^{+++} and Cl^- ions, respectively. The above three reactions will therefore be more correctly represented if we write the equations

(4) $Mg + 2\,H^+ + 2\,Cl^- = Mg^{++} + 2\,Cl^- + H_2$

(5) $Zn + 2\,H^+ + SO_4^{--} = Zn^{++} + SO_4^{--} + H_2$

(6) $2\,Al + 6\,H^+ + 6\,Cl^- = 2\,Al^{+++} + 6\,Cl^- + 3\,H_2$

If we examine these latter reactions carefully we will find that, in reaction (4) for instance, nothing apparently happens to the 2 Cl^- ions; they are present in the acid solution at the start and they are still present in the salt solution. What happens, apparently, is that magnesium metal goes into solution to form Mg^{++} ions, and in so doing it replaces the hydrogen ions and causes them to be liberated as hydrogen gas; the Cl^- ions appear not to be involved in the reaction. The essential reaction for what takes place can therefore be represented by the *net ionic equation*

$$Mg + 2\,H^+ = Mg^{++} + H_2 \tag{7}$$

Likewise, in equation (5), the SO_4^{--} ion appears to have no active part in the reaction, since it is present in the acid at the start and is also present in the solution of the salt at the finish. The net ionic equation for reaction (5) will then be

$$Zn + 2\,H^+ = Zn^{++} + H_2 \tag{8}$$

By the same reasoning the net ionic equation for reaction (6) will be

$$2\,Al + 6\,H^+ = 2\,Al^{+++} + 3\,H_2 \tag{9}$$

Note that these ionic equations must balance with respect to total charges on the ions as well as with respect to the number of atoms of each element.

Looking back over equations (7), (8), and (9), we conclude that the reaction of a metal with an acid to liberate hydrogen involves, in every instance, the reaction of the metal with hydrogen ions to give hydrogen gas and the metal ion. One cannot go so far as to say that the anion of the acid can be left out of the picture entirely. To have a reaction at all we must have an acid; and to have hydrochloric and sulfuric acids we must have Cl^- and SO_4^{--} ions as well as H^+ ions. Furthermore, if the solutions obtained in the three reactions are evaporated to dryness, solid $MgCl_2$, $ZnSO_4$, and $AlCl_3$, respectively, will be recovered, and these salts cannot exist without the Cl^- and SO_4^{--} ions being included.

If the reaction of a metal, Mg for instance, with a dilute acid is in fact correctly represented by the equation

$$Mg + 2\,H^+ = Mg^{++} + H_2 \tag{10}$$

then, in accordance with what has been said in Chapter 10, the rate of the reaction should be proportional to the concentration of hydrogen ions. That this is true was shown in the laboratory work accompanying the discussion of hydrogen in Chapter 4. Magnesium, it was found, liberates hydrogen much more rapidly from 1 *M* HCl than from

1 M $HC_2H_3O_2$. Acetic acid we learned in 12.4 is a very weak acid; only a small per cent of its molecules are ionized. Therefore the concentration of hydrogen ions in 1 M $HC_2H_3O_2$ is low and the rate at which these hydrogen ions will react with magnesium will be very slow. On the other hand, HCl is a very strong acid, so its 1 M solution contains a high concentration of H^+ ions. It should therefore react with Mg much more rapidly than acetic acid; and it does.

In the only other type of reaction in solution that we have encountered to date in which an electrolyte was involved, a metal (Zn) reacted with a solution of the salt of a less active metal. The molecular equation or formula equation for this reaction is

$$Zn + CuSO_4 = ZnSO_4 + Cu \tag{11}$$

The net ionic equation is

$$Zn + Cu^{++} = Zn^{++} + Cu \tag{12}$$

Additional ionic equations will be given in Chapter 13.

12.7 Equilibrium in ionization of weak electrolytes. We have learned that:

1. Solutions of electrolytes contain oppositely charged ions ($HCl = H^+ + Cl^-$).

2. All weak electrolytes are incompletely ionized; their solutions contain un-ionized molecules as well as ions.

It is entirely probable, therefore, that the ionization of a weak electrolyte may be a reversible process, that the un-ionized molecules may be in equilibrium with their ions, and that the ionization reaction for a weak electrolyte such as $HC_2H_3O_2$ should be represented by the equation

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^- \tag{1}$$

If the ionization reaction does reach a state of equilibrium as represented by the above equation it should be possible to shift the equilibrium in exactly the same manner as in a molecular equilibrium process (see 10.5). Thus if the concentration of $C_2H_3O_2^-$ ions in a molar solution of acetic acid is increased, the equilibrium in reaction (1) should be shifted to the left. The net result of this equilibrium shift will be that (a) the concentration of un-ionized $HC_2H_3O_2$ molecules will be increased, and (b) the concentration of H^+ ions will be decreased. The relative concentration before and after adding the $C_2H_3O_2^-$ ions can be pictorialized as follows:

(2) Before: $HC_2H_3O_2 \rightleftarrows H^+ \times C_2H_3O_2^-$

(3) After: $HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-$

That such an equilibrium shift actually does take place when $C_2H_3O_2^-$ ions are added to acetic acid can be proved by the following experiment. Place 100 ml of 1 *M* $HC_2H_3O_2$ in each of two flasks. To one flask add some solid sodium acetate ($NaC_2H_3O_2$) and mix until the salt is dissolved. Since $NaC_2H_3O_2$ is a salt and hence a strong electrolyte, its addition is equivalent to adding $C_2H_3O_2^-$ ions. If now identical large pieces of magnesium (more than enough metal to react with all the acid) are dropped into each flask, it will be observed that the acid to which $NaC_2H_3O_2$ has been added liberates hydrogen more slowly than does the one to which no acetate ions were added. This, in accordance with what has been stated in 12.6, shows that the concentration of hydrogen ions in the solution to which acetate ions have been added is less than that in the other solution. This in turn shows that the equilibrium in the ionization reaction has been shifted by addition of acetate ions; therefore the reaction must have reached a state of equilibrium in the first place. Equation (1) gives, therefore, a correct picture of the reaction. A shift in the equilibrium of an ionization reaction caused by increasing the concentration of an ion involved in the equilibrium, such as takes place when acetate ions are added to acetic acid, is referred to as a *common ion effect.*

Further evidence that the ionization of acetic acid is a reversible reaction which reaches a state of equilibrium is given by the fact that *all* the acid in *each* flask is eventually used up, and the *same quantity* of hydrogen gas is given off from each. That means that all the acetic acid must have changed to H^+ ions and $C_2H_3O_2^-$ ions. The only way to account for this fact is by an equilibrium process such as is represented by equation (1); removal of H^+ ions by reaction with magnesium shifts the equilibrium so far to the right that eventually the concentration of $HC_2H_3O_2$ is reduced to zero and the ionization is complete.

Similar observations with other solutions lead to the conclusion that *the ionization of all weak electrolytes is a reversible process which reaches a state of equilibrium.* A number of specific ionization equilibria will be discussed in Chapters 13 and 14.

12.8 Ionization constants. Ionization equilibria are true chemical equilibria. Therefore the product of the concentration of the ions divided by the concentration of the un-ionized molecules will be a constant at a given temperature. This constant is called the ionization constant and is commonly represented by the notation K_i. Thus for the reaction

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-$$

$$K_i = \frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

As in all applications of the mass law, concentrations are given in moles (gram-ions) per liter.

Since the concentrations of the ions are given in the numerator, it is obvious that a large ionization constant means a high concentration of ions, a high per cent ionization. On the other hand, a low ionization constant means a low per cent ionization and hence a very weak electrolyte.

If an electrolyte yields more than 1 ion of a given species, the concentration of that ion is raised to a power equal to the number of ions. Thus for the ionization

$$H_2SO_3 \rightleftarrows 2\,H^+ + SO_3^{--}$$

the over-all ionization constant is

$$K_i = \frac{[H^+]^2 \times [SO_3^{--}]}{[H_2SO_3]}$$

It should be noted, however, that the ionization of electrolytes that yield more than 1 ion of a given species proceeds in steps. Thus H_2SO_3 first ionizes according to the equation

$$H_2SO_3 \rightleftarrows H^+ + HSO_3^-$$

The HSO_3^-, in turn, ionizes as follows:

$$HSO_3^- \rightleftarrows H^+ + SO_3^{--}$$

The ionization constant for the first step is

$$K_1 = \frac{[H^+] \times [HSO_3^-]}{[H_2SO_3]}$$

and for the second step as

$$K_2 = \frac{[H^+] \times [SO_3^{--}]}{[HSO_3^-]}$$

The over-all ionization constant is the product of K_1 and K_2.

$$K_i = K_1 \times K_2 = \frac{[H^+] \times [HSO_3^-]}{[H_2SO_3]} \times \frac{[H^+] \times [SO_3^{--}]}{[HSO_3^-]}$$

$$= \frac{[H^+]^2 \times [SO_3^{--}]}{[H_2SO_3]}$$

Phosphoric acid ionizes in three stages according to the equations

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$$
$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{--}$$
$$HPO_4^{--} \rightleftarrows H^+ + PO_4^{---}$$

Each step has its own ionization constant.

Table 12.2 lists the ionization constants for a number of weak electrolytes. For the *polyprotic acids* (those that yield more than 1 hydrogen ion) the constants for each stage in the ionization (K_1, K_2, K_3) are given. It should be noted that water is a weak electrolyte with an ionization constant of $1 \times 10^{-14}/55.5$. Water is ionized to such an extent that a liter of pure water at 25° contains 1×10^{-7} gram-ion of H^+ ions and 1×10^{-7} gram-ion of OH^- ions.

TABLE 12.2

IONIZATION CONSTANTS OF WEAK ACIDS AND BASES

Acetic	$HC_2H_3O_2$	1.8×10^{-5}
Arsenic	H_3AsO_4	$K_1 = 2.5 \times 10^{-4}$
		$K_2 = 5.6 \times 10^{-8}$
		$K_3 = 3.0 \times 10^{-13}$
Arsenious	H_3AsO_3	$K_1 = 6.0 \times 10^{-10}$
Boric	H_3BO_3	$K_1 = 6.0 \times 10^{-10}$
Carbonic	H_2CO_3	$K_1 = 4.2 \times 10^{-7}$
		$K_2 = 4.8 \times 10^{-11}$
Chromic	H_2CrO_4	$K_1 = 1.8 \times 10^{-1}$
		$K_2 = 3.2 \times 10^{-7}$
Formic	$HCHO_2$	2.1×10^{-4}
Hydrocyanic	HCN	4.0×10^{-10}
Hydrofluoric	HF	6.9×10^{-4}
Hydrogen sulfide	H_2S	$K_1 = 1.0 \times 10^{-7}$
		$K_2 = 1.3 \times 10^{-13}$
Hypochlorous	HClO	3.2×10^{-8}
Nitrous	HNO_2	4.5×10^{-4}
Oxalic	$H_2C_2O_4$	$K_1 = 3.8 \times 10^{-2}$
		$K_2 = 5.0 \times 10^{-5}$
Phosphoric	H_3PO_4	$K_1 = 7.5 \times 10^{-3}$
		$K_2 = 6.2 \times 10^{-8}$
		$K_3 = 1.0 \times 10^{-12}$
Sulfurous	H_2SO_3	$K_1 = 1.3 \times 10^{-2}$
		$K_2 = 5.6 \times 10^{-8}$
Ammonium hydroxide	NH_4OH	1.8×10^{-5}
Water	HOH	$\frac{1.0 \times 10^{-14}}{55.5}$

12.9 Nonaqueous solutions. The discussion in this book will be confined to aqueous solutions of electrolytes. It should be noted, how-

ever, that solvents other than water yield ionic solutions. Reactions in liquid ammonia and liquid HF have been widely studied and will be encountered in later courses.

It should also be pointed out that every solvent has its own characteristic freezing point and boiling point constant. As in the case of water, the constant represents the number of centigrade degrees that the freezing point is lowered and the boiling point is raised when 1 mole of solute is dissolved in 1000 g of solvent, that is, in a 1 molal solution. The molal freezing point constant for acetic acid is 3.9°, for benzene is 5.1°, for naphthalene is 6.8°, and for camphor is 39.8°. As in the case of water, all molal freezing point and boiling point constants are only approximately "constant"; there is some slight variation from one nonelectrolyte solute to another.

Questions and Problems

1. Define or describe and illustrate: electrolyte; nonelectrolyte; boiling point constant; freezing point constant; ion; cation; anion; ionization; dissociation; strong electrolyte; weak electrolyte; gram-ion; hydronium ion; cathode; anode; valence; strong acid; weak acid; strong base; weak base; net ionic equation; common ion effect; ionization constant.

2. Why does salt cause ice to melt?

3. Why is salt applied to the ice when freezing ice cream in a small home freezer?

4. Account for the fact that addition of solid $NaC_2H_3O_2$ to 100 ml of 0.1 M $HC_2H_3O_2$ decreases the rate at which hydrogen gas is evolved by reaction with excess magnesium, but does not alter the total amount of gas given off.

5. When are the ions that are present in solutions of electrolytes formed?

6. When covalent SO_2 gas is dissolved in water an ionic solution is formed. Point out the reactions that take place.

7. Cite the evidence which indicates that ions are present in solutions of electrolytes.

8. How would you determine experimentally whether an electrolyte is weak or strong?

9. How can the per cent ionization of a weak electrolyte be determined? Explain in detail.

10. Write the net ionic equation for the reaction that takes place when aluminum reacts with dilute sulfuric acid.

11. How could you demonstrate experimentally that the ionization of the weak acid H_2SO_3 is a reversible reaction?

12. Eight grams of the nonelectrolyte C_2H_5OH were dissolved in 400 g of water. Calculate the freezing point of the solution.

13. When 12 g of a nonelectrolyte were dissolved in 300 g of water, the resulting solution froze at -1.62°C. What was the approximate molecular weight of the nonelectrolyte? Why does the answer represent an approximate molecular weight rather than an exact weight?

14. How many grams of $C_3H_5(OH)_3$, a nonelectrolyte, must be dissolved in 600 g of water to give a solution which will freeze at -4°C?

15. When 5.12 g of the non-ionizing solute naphthalene ($C_{10}H_8$) are dissolved in 100 g of carbon tetrachloride (CCl_4), the boiling point of the CCl_4 is raised 2°C. Calculate the molal boiling point constant for CCl_4.

CHAPTER 13

Acids, Bases, Salts

All acids, bases, and salts are electrolytes. With a few exceptions all electrolytes are either acids, bases, or salts (see Table 12.1). It is therefore desirable that, before going further, we learn more about these three classes of substances, how they can be identified, how they can be prepared, and how they react. Not only will such a study give specific information about acids, bases, and salts, but it will give us general information about reactions involving electrolytes.

13.1 Properties of acids. An electrolyte does not display its properties as an electrolyte until it is dissolved in an ionizing solvent such as water, liquid NH_3, liquid SO_2, liquid HF, etc. Since in this book we are considering only water solutions, it can be stated that, to show the properties of an acid, an acidic substance must be in water solution. Strictly speaking, an acid does not exist except in solution. It is common practice, however, to refer to dry HCl gas, pure liquid H_3PO_4, and solid H_3BO_3 as hydrochloric acid, phosphoric acid, and boric acid, respectively; the implication is that they have all the essential constituents of an acid and will each yield an acid when dissolved in water.

The properties listed below are displayed only by water solutions of the acids. Extremely weak acids will not display all these properties.

1. *They contain* H^+ *ions.* All the unique properties of acids are due to these H^+ ions. As has already been noted the hydrogen ion, or *proton* as it is also called, is undoubtedly hydrated; this is commonly shown by writing its formula $H_2O \cdot H^+$ or H_3O^+ and referring to it as an hydronium ion, hydrated hydrogen ion, or hydrated proton.

2. *They contain a nonmetal or nonmetal-radical negative ion* (anion). This anion identifies the acid and gives it its characteristic name. Table 13.1 lists the names and formulas of the more common acids that will be encountered in this book, and gives the names and valences (charges) of the anions. Note that the chemical name of the acid identifies the name of the anion, while the formula of the acid indicates the formula and charge (valence) of the anion.

3. *They have a sour taste.* The intensity of the sour taste decreases as the concentration of hydrogen ions decreases. Sour fruits such as lemons,

TABLE 13.1

COMMON ACIDS

Formula	Chemical names		Formula of acid radical (anion)	Name of acid radical	Strength of acid
HCl	Hydrogen chloride	hydrochloric	Cl^-	chloride	strong
HBr	Hydrogen bromide	hydrobromic	Br^-	bromide	strong
HI	Hydrogen iodide	hydriodic	I^-	iodide	strong
HNO_3	Hydrogen nitrate	nitric	NO_3^-	nitrate	strong
H_2SO_4	Hydrogen sulfate	sulfuric	SO_4^{--}	sulfate	strong
$HC_2H_3O_2$	Hydrogen acetate	acetic	$C_2H_3O_2^-$	acetate	weak
HF	Hydrogen fluoride	hydrofluoric	F^-	fluoride	weak
H_2SO_3	Hydrogen sulfite	sulfurous	SO_3^{--}	sulfite	weak
H_2CO_3	Hydrogen carbonate	carbonic	CO_3^{--}	carbonate	weak
H_3PO_4	Hydrogen phosphate	phosphoric	PO_4^{---}	phosphate	weak
H_3BO_3	Hydrogen borate	boric	BO_3^{---}	borate	weak
H_2S	Hydrogen sulfide	hydrosulfuric	S^{--}	sulfide	weak
H_2SiO_3	Hydrogen silicate	silicic	SiO_3^{--}	silicate	weak

grapefruit, gooseberries, cherries, and green apples owe their sour taste to the presence of acids.

4. *They turn blue litmus paper red.* Litmus is one of a large number of *indicators* that show characteristic colorations in the presence of acids. Table 14.2 lists a number of these indicators.

5. *They liberate hydrogen gas when treated with an active metal.* The *molecular equations* for the reaction of magnesium with typical acids are

$$Mg + 2\,HCl \text{ (hydrochloric)} = H_2 + MgCl_2 \text{ (magnesium chloride)}$$
$$Mg + H_2SO_4 \text{ (sulfuric)} = H_2 + MgSO_4 \text{ (magnesium sulfate)}$$
$$Mg + 2\,HBr \text{ (hydrobromic)} = H_2 + MgBr_2 \text{ (magnesium bromide)}$$

The type of reaction illustrated by these three equations is called *replacement;* one element replaces another. The *detailed ionic equations,* giving all species present in the reacting solution are

$$Mg + 2\,H^+ + 2\,Cl^- = Mg^{++} + 2\,Cl^- + H_2$$
$$Mg + 2\,H^+ + SO_4^{--} = Mg^{++} + SO_4^{--} + H_2$$
$$Mg + 2\,H^+ + 2\,Br^- = Mg^{++} + 2\,Br^- + H_2$$

The *net equation,* obtained by canceling out the species that occur on both sides of the equation, and giving therefore only the formulas of the species that are actually involved in the reaction, will be the same for all three reactions.

$$Mg + 2\,H^+ = Mg^{++} + H_2$$

The *word equation* for the reaction of any active metal with any acid will be

metal + hydrogen ion = metal ion + hydrogen gas

The hydrogen gas that is liberated can be identified by seeing if its mixture with air will explode when ignited (sec 4.2).

6. *They react with bases to form salts and water.* We have learned that solutions of bases all contain OH^- ions (see Table 12.1). The essential feature of the reaction between a base and an acid is the combination of the H^+ ions of the acid with the OH^- ions of the base to form H_2O. Because the acid contributes the hydrogen ion in this reaction it is referred to as a *proton donor.* The base is the *proton acceptor.* Since the properties of an acid are due to the H^+ ions, while the properties of a base are due to the OH^- ions, combination of H^+ ions with OH^- ions destroys the characteristic properties of each. For that reason it is referred to as *neutralization.* Some typical *molecular equations* are

$$NaOH \text{ (sodium hydroxide)} + HI = NaI + H_2O$$
$$2\,KOH \text{ (potassium hydroxide)} + H_2SO_4 = K_2SO_4 + 2\,H_2O$$
$$Ca(OH)_2 \text{ (calcium hydroxide)} + 2\,HNO_3 = Ca(NO_3)_2 + 2\,H_2O$$

The above three reactions illustrate *double replacement* (double decomposition). One element or radical in one compound takes the place of one element or radical in the other; no oxidation-reduction occurs.

The *detailed ionic equations* for these three reactions are

$$Na^+ + OH^- + H^+ + I^- = Na^+ + I^- + H_2O$$
$$2\,K^+ + 2\,OH^- + 2\,H^+ + SO_4^{--} = 2\,K^+ + SO_4^{--} + 2\,H_2O$$
$$Ca^{++} + 2\,OH^- + 2\,H^+ + 2\,NO_3^- = Ca^{++} + 2\,NO_3^- + 2\,H_2O$$

The *net equation* will be the same for each reaction except that the number of moles of H^+, OH^- and H_2O will be different in the first.

$$H^+ + OH^- = H_2O$$

This net equation emphasizes the fact that the essential reaction in the neutralization of an acid by a base is the combination of H^+ ions with OH^- ions to form water.

7. *They liberate* CO_2 *gas when treated with the carbonate of a metal.* Salts and water are the other products. Typical *molecular equations* are

$$Na_2CO_3 + 2\,HCl = 2\,NaCl + H_2O + CO_2\uparrow$$
$$K_2CO_3 + H_2SO_4 = K_2SO_4 + H_2O + CO_2\uparrow$$
$$(NH_4)_2CO_3 + 2\,HBr = 2\,NH_4Br + H_2O + CO_2\uparrow$$

The *detailed ionic equations* are

$$2\,Na^+ + CO_3^{--} + 2\,H^+ + 2\,Cl^- = 2\,Na^+ + 2\,Cl^- + H_2O + CO_2\uparrow$$
$$2\,K^+ + CO_3^{--} + 2\,H^+ + SO_4^{--} = 2\,K^+ + SO_4^{--} + H_2O + CO_2\uparrow$$
$$2\,NH_4^+ + CO_3^{--} + 2\,H^+ + 2\,Br^- = 2\,NH_4^+ + 2\,Br^- + H_2O + CO_2\uparrow$$

The *net equation*, which is the same for each reaction is

$$CO_3^{--} + 2\,H^+ = H_2O + CO_2\uparrow$$

It should be noted that the carbonates of metals are typical salts and that the reactions given above are specific examples of the *general equation*

$$\text{salt} + \text{acid} = \text{salt} + \text{acid}$$

The acid that is formed in this particular case (H_2CO_3) is unstable and decomposes to give water and an insoluble gas (see Table 11.3). The escape of the CO_2 gas causes the reaction to be complete to the right (see 10.7).

It should be stated that, in a broader sense, an acid may be defined as any substance which contributes protons for reactions with other substances. The H^+ (or H_3O^+) ion is the prime acid in aqueous systems; but an ion such as NH_4^+ is also acidic, since it contributes a proton to the OH^- ion in the reaction

$$NH_4^+ + OH^- = NH_3 + H_2O$$

13.2 Molecular equations, detailed ionic equations, and net equations. Prior to Chapter 12 equations for all reactions were written in molecular form. These equations could suggest that all reactions involved molecules or took place between molecules. Since many of the reactants do not exist as molecules, this obviously cannot always be true.

We learned, in Chapter 12, that electrolytes are dissociated into ions and that when solutions of electrolytes react the reacting units are ions. This fact was represented in Section 12.6 by the use of *ionic equations*. In Section 13.1 the reactions illustrating the chemical properties of acids were written in *detailed ionic* and *net ionic* form; the *molecular* equation for each reaction was also included so that it could be compared with the two ionic forms.

It is not the intention to write the equations for all future reactions involving electrolytes in solution in these three different ways; normally, the equation for a specific reaction will be written only one way. The question will be, which way? In arriving at the answer to this question

it is fair to assume that the ideal equation for a reaction should be (1) *as simple as possible,* and (2) *as informative as possible.*

An examination of the equations given in 13.1 will show that the net equation is in each case the simplest. A similar examination of hundreds of additional equations would reveal that the net equation is always simpler than the detailed ionic equation and is generally simpler than the molecular equation; the only time that it is not simpler than the molecular equation is when the two are identical.

Simplicity is, however, of secondary importance. First and foremost the equation should conform to recognized experimental facts; at the same time it should give that information which seems *most pertinent* to the reaction under consideration. Just how the three ways of writing an equation compare on these two points can best be judged by expressing specific reactions in each way.

1. *The gas-phase reaction of* CO *with* H_2O (*steam*) *to give* CO_2 *and* H_2. All reaction is believed to take place between molecules. Therefore there is only one way to write the equation, namely, molecular.

$$CO + H_2O = CO_2 + H_2$$

When all reactants and products are molecules, the equation is always written in the molecular form. This molecular equation makes no pretense of giving the mechanism by which the reaction takes place except to state that molecules are the reacting species. It gives the exact mole ratios of reactants and products: in other words, it gives the correct *stoichiometry* of the reaction. It should be noted that nonelectrolytes always exist in solution as molecules.

2. *Neutralization of a solution of a strong acid* (HCl) *by a solution of a strong base* (NaOH). Both reactants are strong electrolytes; therefore the reaction is between ions. One of the products, NaCl, is a salt and therefore a strong electrolyte; the other product, water, is a weak electrolyte. The equation for this reaction can be, and very commonly is, written in either molecular, detailed ionic, or net form.

The *molecular equation* for this reaction is

$$NaOH + HCl = NaCl + H_2O$$

This obviously does not conform to the recognized fact that reaction involving electrolytes is between ions. It makes no pretense whatever of giving the mechanism of the reaction; in particular it does not pretend that "molecules" of NaOH react with "molecules" of HCl. All it does is give:

(a) The recognized simple chemical formulas of the solid sodium

hydroxide and gaseous hydrogen chloride that were used to prepare the reacting solutions, and of the solid salt that will be recovered and the water that will be driven off when the resulting solution is evaporated to dryness. This, incidentally, is not to be looked upon as unimportant information; in a commercial process or a laboratory experiment, it may be *the* important information.

(b) The correct stoichiometry of the reaction. This enables us to make any desired calculation involving amounts of NaOH, HCl, NaCl, H_2O, Na^+, Cl^-, H^+, or OH^- involved in the reaction.

The detailed ionic equation gives the formulas of all the species present in the reaction system and presents what is believed to be the simple mechanism of the reaction. The detailed ionic equation for the above reaction is

$$Na^+ + OH^- + H^+ + Cl^- = Na^+ + Cl^- + H_2O$$

An examination shows that Na^+ and Cl^- appear on both sides of the equation; they apparently do not take part in the reaction and can therefore be canceled out. That means that the only reaction is the combination of H^+ ions with OH^- ions to form H_2O, according to the *net equation*

$$H^+ + OH^- = H_2O$$

This net equation gives the predominant reacting species, and in this particular reaction *shows how they react.*

3. *Neutralization of a solution of the strong acid* HCl *by the weak base* NH_4OH. (It should be noted at this time that the solution of the weak base NH_4OH is in reality a solution of NH_3 in water. Although there is no positive evidence for the existence of a compound with the simple formula NH_4OH, the use of this formula to designate the weak base formed when NH_3 is dissolved in water has become so general that there would seem to be no good reason for discontinuing it. The solution of NH_3 in water does contain NH_4^+ and OH^- ions. To form these two ions, NH_3 and H_2O must interact in the ratio of 1 mole of NH_3 to 1 mole of H_2O in the manner discussed in Section 12.1. The formula NH_4OH is made up of NH_3 and H_2O in the ratio of 1 mole of NH_3 to 1 mole of H_2O. The important fact to remember is that the formula NH_4OH is used to *represent a solution of* NH_3 *in water.* If we keep this in mind there is nothing inconsistent about using it rather than the notation, "a solution of NH_3 in water" or the formulation, $NH_3 + H_2O$.)

The *molecular equation* for the reaction of HCl with NH_4OH is

$$NH_3 + H_2O + HCl = NH_4Cl + H_2O$$

The *detailed reaction* is represented by the following equations:

(1) $NH_3 + H_2O \rightleftarrows NH_4^+ \times OH^-$ (weak base)

(2) $HCl = H^+ + Cl^-$ (strong acid)

(3) OH^- [from equation (1)] + H^+ [from equation (2)] = H_2O

Since NH_4OH is a weak base, the concentration of NH_3 molecules in equation (1) is very high, while the concentration of NH_4^+ and OH^- ions is very low. In contrast, the strong acid HCl is completely ionized and gives a very high concentration of H^+ and Cl^- ions in equation (2). Reaction (3) is complete because H_2O is a very weak electrolyte. The combination, in equation (3), of OH^- ions from equation (1) and H^+ ions from equation (2) causes reaction (1) to be complete to the right. The net product of the three reactions is a solution containing H_2O molecules and NH_4^+ and Cl^- ions.

In writing the *net equation* for this reaction one should note that NH_3 molecules predominate in the solution of ammonium hydroxide, while H^+ and Cl^- ions predominate in the solution of hydrochloric acid. The predominant reacting species are therefore NH_3 molecules and H^+ and Cl^- ions, and the product species are NH_4^+ and Cl^- ions as expressed in the equation

$$NH_3 + H^+ + Cl^- = NH_4^+ + Cl^-$$

Since Cl^- ions appear on both sides of this equation, they apparently do not react, and can therefore be canceled. This leaves the *net equation*

$$NH_3 + H^+ = NH_4^+$$

This equation gives the *predominant reacting species*. It does not pretend to give the mechanism of the reaction. When two strong electrolytes react, as in the previous illustration, the net equation may, in fact, give the accepted mechanism of the reaction; usually, however, it is interested only in the over-all behavior of the predominant reacting species.

4. *The reaction of a strong acid* (HNO_3) *with the water-insoluble carbonate of a metal* ($CaCO_3$). The *molecular equation* for this reaction is

$$CaCO_3 + 2\,HNO_3 = Ca(NO_3)_2 + H_2O + CO_2\uparrow$$

In representing the *detailed equation* we must recognize that every so-called "insoluble" salt is slightly soluble; since it is a salt, has an ionic crystal lattice, and hence is a strong electrolyte, the soluble portion will be completely ionized. A saturated solution is ultimately formed when a solid dissolves in a liquid; therefore these ions will be in equilibrium with the solid salt. In the case of $CaCO_3$ this fact is represented by the equation

(1) $CaCO_3 \rightleftarrows Ca^{++} + CO_3^{--}$

The complete ionization of the strong acid, HNO_3, is represented by the equation

(2) $$HNO_3 = H^+ + NO_3^-$$

The CO_3^{--} ions from equation (1) react with the H^+ ions from equation (2) according to equation (3).

(3) $$CO_3^{--} + 2\,H^+ = H_2O + CO_2\uparrow$$

Equation (3) represents a complete reaction because CO_2 escapes as a gas, and also because H_2O is a very weak electrolyte. Because reaction (3) is complete, reaction (1), which supplies the CO_3^{--} ions, will be made complete. That means that, if enough HNO_3 is added, the $CaCO_3$ will all dissolve.

In arriving at the net equation we note that solid $CaCO_3$ is a predominant species; *solid reactants or products are always one of the predominant species.* We note also that nitric acid is really a solution of H^+ and NO_3^- ions. If we express these facts in the form of an equation we get

$$CaCO_3 + 2\,H^+ + 2\,NO_3^- = Ca^{++} + 2\,NO_3^- + H_2O + CO_2\uparrow$$

The $2\,NO_3^-$ can be canceled from both sides of the equation. This leaves the *net equation*

$$CaCO_3 + 2\,H^+ = Ca^{++} + H_2O + CO_2\uparrow$$

Summarizing what has been brought out in these illustrations, it can be stated that, in a reaction involving solutions of electrolytes:

1. *The molecular equation makes no effort to show any reacting species.* It does not pretend to show the mechanism of the reaction. (The term "molecular equation" is not a completely satisfactory one since it might imply that a reactant or product exists as molecules; electrovalent compounds do not exist as molecules. Terms such as "formula equation" or "stoichiometric equation" are less satisfactory because they imply that the other two categories are not stoichiometric or do not represent the formulas of the reactants.)

2. *The detailed ionic equation shows all species involved in the reaction,* and gives the simple mechanism by which they react.

3. *The net equation shows only the predominant reacting and product species.* It is not concerned about the mechanism of the reaction although it may sometimes represent it.

4. Since all three equations are balanced, they all represent the correct stoichiometry of the reaction.

General chemistry is concerned more with the identity of the sub-

stances that react and the products that are formed than it is with the detailed process by which the reaction goes on. For that reason net equations are the desired kind and will generally be used for all reactions in solution. Detailed ionic equations will be used when the simple mechanism of a reaction is being discussed. Reactions that do not take place in water solution will be represented by molecular equations, as will reactions involving nonelectrolytes. When it is important to show what product will be recovered when the reaction solution is evaporated to dryness, molecular equations or modified net equations will be used even though the reaction involves soluble strong electrolytes.

In writing the net equation for a reaction in solution it is necessary to decide whether the predominant reacting species are ions or molecules. This decision is made relatively simple by the following rule:

For all soluble strong electrolytes their ions are the predominant species (their "molecules" do not exist in solution); for all other substances their molecules are the predominant species. This means that, for the following substances, the molecules of the substance are the predominant reacting species:

1. All weak electrolytes
2. All insoluble strong electrolytes such as $CaCO_3$, $BaSO_4$, $Al(OH)_3$, etc.
3. All nonelectrolytes

The common strong and weak electrolytes are listed in Section 12.4. This listing can be summarized briefly as follows:

1. With very few exceptions, all salts are strong electrolytes.
2. The acids H_2SO_4, HNO_3, HCl, HBr, and HI are the only strong common acids; all other acids usually encountered are weak.
3. The hydroxides of all metals of group IA and IIA except Mg and Be are strong bases. The hydroxides of all other metals (Be and Mg included) are so sparingly soluble that they are classed as weak bases.
4. Ammonium hydroxide (NH_4OH) is the only common soluble weak base.
5. Water is a very weak electrolyte.

Tables 11.2 and 11.3, pages 222 and 223, give the rules relating to the solubilities of various substances. It should be noted that:

1. All acids normally encountered, except H_2S and H_2CO_3, are very soluble; H_2CO_3 is unstable and yields insoluble CO_2 as a gaseous product.
2. Ammonium hydroxide and the hydroxides of all group IA and IIA metals except Be and Mg are soluble; all other metal hydroxides are insoluble.
3. There is no simple rule concerning the solubility of salts; all the rules given in Table 11.2 must be applied.

Using the above rules as our guide, we can write the following illustrative *net equations* for reactions involving solutions of acids. Each equation is supplemented by a statement of the information which the equation gives about the reaction.

(1) $$Cu(OH)_2 + 2\,H^+ = Cu^{++} + 2\,H_2O$$

The insoluble base $Cu(OH)_2$ reacts with a strong acid to form a soluble salt and the weak electrolyte, water.

(2) $$OH^- + HC_2H_3O_2 = C_2H_3O_2^- + H_2O$$

A strong base reacts with the weak acid, $HC_2H_3O_2$, to form a soluble salt and water.

(3) $$CO_3^{--} + 2\,H^+ = H_2O + CO_2\uparrow$$

A soluble carbonate of a metal reacts with a strong acid to form a soluble salt, the insoluble gas CO_2, and the weak electrolyte H_2O.

(4) $$NH_3 + HCN = NH_4^+ + CN^-$$

The weak base NH_4OH reacts with the weak acid HCN to form a soluble salt and water.

(5) $$Ba^{++} + 2\,OH^- + 2\,H^+ + SO_4^{--} = BaSO_4 + 2\,H_2O$$

The strong base $Ba(OH)_2$ reacts with the strong acid H_2SO_4 to form the insoluble salt $BaSO_4$ and water.

(6) $$6\,K + 2\,H_3PO_4 = 6\,K^+ + 2\,PO_4^{---} + 3\,H_2\uparrow$$

The metal K reacts with a solution of the weak acid H_3PO_4 to liberate hydrogen and form a soluble salt. If the solution is evaporated to dryness, solid K_3PO_4 will be recovered.

It is obvious from these examples that, in addition to being simple, a net equation gives a lot of information about a reaction. The net equation is always used in determining the equilibrium constant for a reaction in solution.

It should be emphasized that one can seldom be absolutely certain, beyond the shadow of a doubt, that the choice of predominant reacting species in a net equation or of specific steps in a set of detailed reactions is the correct one. The best that one can do is to make the selection that is most consistent with the known experimental facts.

13.3 Ways in which acids may be classified

1. *Strong*, such as HCl, HBr, HI, H_2SO_4, and HNO_3; *weak*, such as $HC_2H_3O_2$, H_2SO_3, H_3PO_4, H_2S, H_2CO_3, and HF. A strong acid is com-

pletely ionized; a weak acid is slightly ionized. The stronger the weak acid, the more highly it is ionized, the greater the H^+ ion concentration in solutions which contain, potentially, the same concentration of total acid hydrogen (1 mole of H_2S contains twice the amount of potential hydrogen as 1 mole of HCN). The strength of an acid can be determined by:

(a) *Measuring the electric conductivity of a solution of definite concentration.* The stronger the acid the greater the conductivity. This is an exact, quantitative method; it depends on the fact that the conductivity of a solution is proportional to the concentration of its ions (see 12.5).

When comparing the strengths of two acids by any of the methods given in this section, the concentrations of the two acids must be equivalent. That means that the number of gram-atoms of total hydrogen (H^+ ions plus the hydrogen atoms present in the un-ionized acid) per liter of solution must be the same. To illustrate, 1 *M* HCl is equivalent in concentration to 0.5 *M* H_2SO_4; each solution contains 1 gram-atom of hydrogen per liter.

(b) *Measuring the rate of evolution of hydrogen when the solution is treated with an active metal.* The stronger the acid, the more rapid the rate. This is not an exact method.

(c) *Measuring the rate of evolution of* CO_2 *when the acid is added to a carbonate.* The stronger the acid, the more rapid the rate. This is not an exact method.

(d) *Measuring the freezing point, or* in some cases *the boiling point, of a solution of the acid of known molality.* The details of this method are discussed in Section 12.5.

2. *Binary* (two elements), such as HCl, HBr, HI, HF, and H_2S; *ternary* (three elements), such as H_2SO_4, H_2SO_3, H_2CO_3, HNO_3, and H_3PO_4.

3. *Nonvolatile* (high boiling point, not readily vaporized) such as H_2SO_4 and H_3PO_4; *volatile* (high vapor pressure, low boiling point) such as HCl, HBr, HI, HF, and H_2S. Volatility is relative; HNO_3 is volatile by comparison with H_2SO_4 but nonvolatile by comparison with HCl. Likewise, HCl is more volatile than H_2SO_4, but its high solubility in water renders it relatively nonvolatile by comparison with H_2S, which is only slightly soluble in water.

Certain acids are unstable and yield volatile products. Thus H_2CO_3 decomposes to give H_2O and CO_2 (gas), while H_2SO_3 decomposes to form H_2O and SO_2 (gas).

4. *Monohydrogen* (monoprotic, monobasic) such as HCl, HBr, HI, HF, and HNO_3; *polyhydrogen* (dihydrogen, trihydrogen, polyprotic,

dibasic, tribasic) such as H_2SO_4, H_3PO_4, H_2SO_3, H_3AsO_4, H_2S, and H_2CO_3. The term *monobasic* signifies that 1 mole of the acid contains enough replaceable hydrogen, or can yield enough H^+ ions, to react with 1 mole of the basic OH^- ion; a mole of dibasic acid yields enough H^+ ions to react with 2 moles of OH^- ions. The term *monoprotic* signifies that 1 molecule yields 1 proton (H^+ ion).

5. *Ortho and meta.* A *meta* acid generally differs from the corresponding *ortho* acid by 1 molecule of water per molecule, and can generally be converted to the ortho acid by the addition of water.

meta acid		*ortho acid*
HBO_2	$+ H_2O =$	H_3BO_3
HPO_3	$+ H_2O =$	H_3PO_4
H_2SiO_3	$+ H_2O =$	H_4SiO_4

13.4 Formation of acids

1. *Hydrogen + a nonmetal = binary acid*

$$H_2 + Cl_2 \text{ (heated)} = 2\,HCl$$
$$H_2 + F_2 \text{ (heated)} = 2\,HF$$
$$H_2 + Br_2 \text{ (heated)} = 2\,HBr$$

This illustrates the tendency of nonmetals to form stable binary hydrogen compounds. These compounds are covalent; when dissolved in water they yield a solution of the acid. They illustrate the fact that nonmetals are acid-forming elements.

2. *Oxide of a nonmetal + water = ternary acid*

$$SO_2 + H_2O = H_2SO_3$$
$$SO_3 + H_2O = 2\,H^+ + SO_4^{--}$$
$$P_4O_{10} + 6\,H_2O = 4\,H_3PO_4$$
$$CO_2 + H_2O = H_2CO_3$$

The nonmetal oxide is the *acid anhydride* of the acid which it yields. The acid anhydride may be derived, formulawise, from the acid by removing enough water to eliminate all the hydrogen. Thus

$$H_2SiO_3 - H_2O = SiO_2$$
$$H_4SiO_4 - 2\,H_2O = SiO_2$$
$$2\,H_3AsO_4 - 3\,H_2O = As_2O_5$$
$$2\,HClO_4 - H_2O = Cl_2O_7$$
$$2\,HClO - H_2O = Cl_2O$$

3. *Salt + a nonvolatile acid = new salt + a volatile acid*

$$2\,NaCl + H_2SO_4 \text{ (conc. heated)} = Na_2SO_4 + 2\,HCl\uparrow$$
$$Ca(NO_3)_2 + H_2SO_4 \text{ (conc. heated)} = CaSO_4 + 2\,HNO_3\uparrow$$
$$3\,KBr + H_3PO_4 \text{ (heated)} = K_3PO_4 + 3\,HBr\uparrow$$
$$CaCO_3 + 2\,H^+ + 2\,Cl^- = Ca^{++} + 2\,Cl^- + H_2O + CO_2\uparrow$$
$$Na_2SO_3 + 2\,H^+ + 2\,Cl^- = 2\,Na^+ + 2\,Cl^- + H_2O + SO_2\uparrow$$

In the last two reactions the acids formed (H_2CO_3 and H_2SO_3) are unstable and decompose to give the gaseous anhydrides (CO_2 and SO_2) and water. If these anhydrides are dissolved in water, solutions of the acids (H_2CO_3 and H_2SO_3) will be formed.

This method is used for laboratory preparation of all common acids except the nonvolatile acids H_2SO_4 and H_3PO_4.

The above reactions are referred to as *double replacement* or *double decomposition* reactions because the metal of the salt and the hydrogen of the acid exchange places.

4. *Hydrolysis of nonmetal halides*

$$PBr_3 + 3\,H_2O = H_3PO_3 + 3\,HBr\uparrow$$
$$PI_3 + 3\,H_2O = H_3PO_3 + 3\,HI\uparrow$$
$$SiCl_4 + 4\,H_2O = H_4SiO_4 + 4\,HCl\uparrow$$
$$AsCl_3 + 3\,H_2O = H_3AsO_3 + 3\,HCl\uparrow$$

Hydrolysis as illustrated above is a double replacement reaction in which H_2O is one of the reactants.

Note that two acids are formed. The fact that nonmetals are acid-forming elements is illustrated.

5. Special methods for preparing specific acids. These will be presented when the particular acid is discussed.

13.5 Properties of bases. In line with what has already been said about acids, a basic substance must be in water solution before it will display all the properties enumerated below. Strictly speaking, a base does not exist except in solution. However, solid metal oxides and hydroxides are commonly referred to as bases, the implication being that they will dissolve in water to form bases.

1. *They contain* OH^- *ions.* All the unique properties of bases are due to these OH^- ions.

Attention has already been called to the fact (see 12.8) that water is a weak electrolyte and that a liter of pure water contains 1×10^{-7} gram-ion of H^+ ions and 1×10^{-7} gram-ion of OH^- ions. That makes water both a very weak acid and a very weak base.

2. *They contain a positive metal ion* (cation). (Ammonium hydroxide contains the cation NH_4^+.) This cation identifies the base (sodium hydroxide, Na^+ and OH^-; calcium hydroxide, Ca^{++} and 2 OH^-). The solid metal oxides and hydroxides are referred to as bases because they dissolve in water to give the cation of the metal and OH^- ions. The metals are accordingly referred to as base-forming elements.

3. *They have a flat taste.*

4. *They turn red litmus paper blue* and show characteristic colorations with other indicators (see Table 14.2). A basic reaction toward an indicator is commonly referred to as an *alkaline* reaction.

5. *They react with acids to form salts and water.* As has already been noted, the essential reaction in this *neutralization* process is the combination of the H^+ ions from the acid with the OH^- ions from the base to form the weak electrolyte, H_2O. The base, or more precisely, the basic OH^- ion, is the *proton acceptor* in this reaction, the acid being the *proton donor*.

13.6 Ways in which bases may be classified

1. *Strong*, such as the hydroxides of all metals in periodic group IA and of Ra, Ba, Sr, and Ca in group IIA; *weak*, such as NH_4OH and all metal hydroxides (and oxides) except those that are strong. The strength of a base is determined by the concentration of OH^- ions; the greater the concentration of OH^- ions, the stronger the base. As a general rule the basic strength of the hydroxide decreases as the electropositivity of the metal decreases (see Table 3.3). This decrease in basic strength with decrease in electropositivity of the metal is probably due largely to the decrease in the size of the metallic ion (cation).

To say that a metal is strongly electropositive means that it readily gives up its valence electron (or electrons) to form a positive ion (cation). It follows from this that the large-diameter cation of a strongly electropositive metal (Na^+, K^+, Ca^{++}, etc.) will not show a strong attraction for electrons or negative ions. Therefore the interionic attraction between these cations and OH^- ions will be small. As a result, relatively few of these OH^- ions will be tied up in the form of ion pairs. The concentration of free OH^- ions will accordingly be high and the solution will be strongly basic. A weakly electropositive metal gives up its valence electrons reluctantly to form cations of relatively small size. These cations will show a strong attraction for OH^- ions, and will therefore tend to tie them up in the form of stable ion pairs. As a result, the concentration of free OH^- ions will be low and the solution will be weakly basic. When the element becomes so weakly electropositive that it is actually electronegative in character (and is classed as a

nonmetal), it attracts the OH^- ions so strongly that it combines with the oxygen by means of covalent bonding. As a consequence the bond between O and H in the OH radical breaks, H^+ ions are liberated, and an acid is formed. Thus, while the electropositive element sodium in NaOH yields Na^+ and OH^- ions, the electronegative element chlorine in HClO will yield ClO^- and H^+ ions. Bases and ternary acids are both hydroxides of elements; the difference between the two lies in the fact that in one case the central atom, being an electropositive metal, has little attraction for OH^- ions and allows them to roam, while in the other case the central atom is a nonmetal, has strong attraction for electrons, and as a result ties up the electronegative oxygen end of the OH^- ion so firmly that the latter dissociates to give H^+ ions.

The decrease in basicity of the hydroxide with decrease in size of the ion probably accounts largely for the fact that, in any *period*, as the atomic number increases (as you go from left to right) the basic strength of the hydroxide decreases. Since, in groups IA and IIA, the ionic diameters and electropositivities increase as the atomic numbers increase (see Sections 7.4 and 7.15), it is not surprising to find that in these *groups* the basic strength of the hydroxide increases as the atomic number of the metal increases.

It should be noted that among the less basic hydroxides there are some exceptions to the rule that the more electropositive the metal, the more basic the hydroxide. Thus $Fe(OH)_2$ is a stronger base than $Zn(OH)_2$ even though Zn is more electropositive than Fe.

As noted above, the strongest bases are formed by the cations of largest diameter. These cations are derived from the most strongly electropositive elements (Cs, Rb, K, Na, and Li) and these elements (metals) fall in group IA. Since solutions of bases are said to be *alkaline* (see Section 13.5–4), the solutions of these strong bases are referred to as *alkalis*, the metals are referred to as the *alkali metals*, and group IA is called the *alkali metal group*. The early alchemists named the oxides of calcium, barium, and strontium *alkaline earths* because these compounds were strongly basic and resembled aluminum oxide, a typical "earth." Accordingly these metals, along with Ra, Be, and Mg, are referred to as the *alkaline earth metals*, and group IIA is called the *alkaline earth group*.

The *strength of a base* can be determined by: (a) measuring the electric conductivity of a solution of known concentration. The greater the conductivity, the greater the strength. (b) Observing the freezing point or boiling point of a solution of known molality as described in 12.5.

2. *Soluble* (NH_4OH and the hydroxides of the group IA metals); *moderately soluble* (hydroxides of Ca, Sr, Ba, Ra); *insoluble* (hydroxides

of all metals other than those given above). As already noted, the solubility in water of the hydroxide of a metal decreases, in a general way, as its basic strength decreases.

3. *Monoacidic* (one basic OH group, such as NH_4OH and the group IA hydroxides); *polyacidic* ($Ca(OH)_2$, $Ba(OH)_2$, $Cr(OH)_3$, $Fe(OH)_3$, etc.). Sodium hydroxide is said to be a monoacidic base because 1 mole will yield enough OH^- ions to neutralize 1 gram-ion of H^+ ions.

13.7 Formation of bases and basic oxides

1. *Metal + oxygen* (heated) = *metal oxide*

$$2\,Ca + O_2 = 2\,CaO$$

All common metals except the noble metals react in this manner.

2. *Active metal + cold water* = H_2 + *metal hydroxide*

$$2\,Na + 2\,H_2O = 2\,Na^+ + 2\,OH^- + H_2$$

All group IA and IIA metals except Mg and Be react with cold water.

3. *Less active metal + steam* = H_2 + *metal oxide*

$$Zn + H_2O = ZnO + H_2$$

Metals more reactive than hydrogen are oxidized by steam at high temperatures.

4. *Oxide of an active metal + water = metal hydroxide*

$$CaO + H_2O = Ca^{++} + 2\,OH^-$$

5. *Soluble salt + soluble base = insoluble base + soluble salt*

Molecular: $FeCl_3 + 3\,NaOH = Fe(OH)_3 + 3\,NaCl$

Net: $Fe^{+++} + 3\,OH^- = Fe(OH)_3$

$Cu^{++} + 2\,OH^- = Cu(OH)_2$

$Al^{+++} + 3\,NH_3 + 3\,H_2O = Al(OH)_3 + 3\,NH_4^+$

13.8 Characterization of a normal salt. A normal salt may be described or characterized in the following ways.

1. It is a compound which yields the characteristic cations of a base and the characteristic anions of an acid.

Salt ions	*Base ions*
$NaCl = \mathbf{Na^+} + \mathbf{Cl^-}$	$NaOH = \mathbf{Na^+} + OH^-$
$K_2SO_4 = \mathbf{2\,K^+} + \mathbf{SO_4^{--}}$	$KOH = \mathbf{K^+} + OH^-$
$CaCO_3 = \mathbf{Ca^{++}} + \mathbf{CO_3^{--}}$	$Ca(OH)_2 = \mathbf{Ca^{++}} + 2\,OH^-$

Acid ions

$$HCl = H^+ + Cl^-$$
$$H_2SO_4 = 2\,H^+ + SO_4^{--}$$
$$H_2CO_3 \rightleftarrows 2\,H^+ + CO_3^{--}$$

2. It may be looked upon as a derivative of an acid in which all the hydrogen has been replaced by a metal.

Acid	*Salt*
HCl	NaCl
H_2SO_4	$ZnSO_4$
H_3PO_4	K_3PO_4

3. It may be looked upon as a derivative of a basic hydroxide (base) in which all the OH has been replaced by nonmetal or nonmetal radical.

Base	*Salt*
NH_4OH	NH_4Br
$Cu(OH)_2$	$CuSO_4$
$Fe(OH)_3$	$Fe_2(SO_4)_3$

4. It is a compound with an ionic crystal lattice. All salts are electrovalent compounds, are ionized in the solid state, and have ionic crystal lattices. Since oxides and hydroxides of metals are electrovalent and have ionic crystal lattices, they would, by the above definition, be classed as salts.

13.9 Physical properties of normal salts

1. *Solubility in water.* Because water is a strongly polar liquid it is a good solvent for salts, all of which are electrovalent. However, the solubilities of specific salts vary greatly. This is indicated by the solubility rules given in Table 11.2.

2. *Melting points.* Because of their ionic crystal structure, salts have relatively high melting points.

13.10 Characterization of an acid salt. Compounds such as $NaHSO_3$, $KHSO_4$, $NaHCO_3$, NaH_2PO_4, and Na_2HPO_4 are classed as acid salts. By comparison with normal salts, which have been characterized in 13.8, they may be described as follows:

1. An acid salt is a compound which yields the characteristic ions of both an acid and a salt. An acid yields H^+ ions and nonmetal anions. A salt yields metal cations and nonmetal anions. An acid salt yields H^+ ions, metal cations, and nonmetal anions.

$NaHSO_3$ (sodium hydrogen sulfite) $= Na^+ + HSO_3^-$

$$HSO_3^- \rightleftarrows H^+ + SO_3^{--}$$

NaH_2PO_4 (sodium dihydrogen phosphate) $= Na^+ + H_2PO_4^-$

$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{--}$$
$$HPO_4^{--} \rightleftarrows H^+ + PO_4^{---}$$

It follows that acid salts (except those derived from very weak acids) have the characteristic properties of an acid (see 13.1).

2. It may be looked upon as a derivative of an acid in which only a part of the hydrogen has been replaced by metal.

Acid	*Normal salt*	*Acid salt*
H_2SO_4	Na_2SO_4	$NaHSO_4$
H_3PO_4	Na_3PO_4	Na_2HPO_4
H_2CO_3	K_2CO_3	$KHCO_3$
H_3PO_4	$Ca_3(PO_4)_2$	$Ca(H_2PO_4)_2$

13.11 Characterization of basic salts. Compounds such as CaOHCl and $AlOHCl_2$ are classed as basic salts. By comparison with normal salts they may be characterized as follows:

1. They are compounds which yield the characteristic ions of both a base and a salt. (OH^-, nonmetal anion, and metal cation)

PbOHCl (basic lead chloride) $= Pb^{++} + OH^- + Cl^-$

$AlOHCl_2$ (basic aluminum chloride) $= Al^{+++} + OH^- + 2\,Cl^-$

There are relatively few basic salts and most of them are insoluble in water.

2. They may be looked upon as derivatives of bases in which only a part of the OH has been replaced by nonmetal.

Base	*Normal salt*	*Basic salt*
$Ca(OH)_2$	$CaCl_2$	CaOHCl
$Bi(OH)_3$	$BiCl_3$	BiOCl

13.12 Formation of normal salts. Detailed equations will be written in all cases where a salt is soluble because the net equation will not show the identity of the salt. All illustrative reactions are complete reactions for one or more of the following reasons: (a) a gas escapes; (b) a precipitate is formed; (c) a weak electrolyte is formed (see 10.7). Formulas for solids and precipitates are given in boldface type.

1. *Replacement reactions.* An element is replaced by a more reactive element.

(a) Metal above hydrogen in electropositivity + dilute acid = salt + H_2

$$\mathbf{Zn} + 2\,H^+ + SO_4^{--} = Zn^{++} + SO_4^{--} + H_2\uparrow$$

In this instance, as in all other methods for preparing salts, if the solution of the salt is evaporated to dryness the solid salt $ZnSO_4$ will be recovered.

(b) Metal + salt of less electropositive metal = less electropositive metal + salt of more electropositive metal

$$\mathbf{Zn} + Cu^{++} + SO_4^{--} = \mathbf{Cu} + Zn^{++} + SO_4^{--}$$

The solid Cu can be filtered off and the $ZnSO_4$ recovered by evaporation.

(c) Halogen + less electronegative halide = less electronegative halogen + halide

$$Cl_2 + 2\,K^+ + 2\,Br^- = 2\,K^+ + 2\,Cl^- + Br_2\uparrow$$

The bromine gas can be boiled off and the KCl recovered by evaporation.

2. *Direct combination*

(a) Metal + nonmetal = binary salt

$$\mathbf{Fe} + \mathbf{S}\ (\text{heated}) = \mathbf{FeS}$$
$$\mathbf{Cu} + Cl_2\ (\text{heated}) = \mathbf{CuCl_2}$$

As a general rule any metal will combine with any nonmetal. The more strongly electropositive the metal and the more strongly electronegative the nonmetal, the greater will be the tendency to interact and the greater will be the heat of formation and stability of the salt.

(b) Oxide of metal + oxide of nonmetal = ternary salt

$$\mathbf{CaO} + CO_2 = \mathbf{CaCO_3}$$

3. *Decomposition of a ternary salt = new salt* + O_2

$$2\,\mathbf{KClO_3}\ (\text{heated}) = 2\,\mathbf{KCl} + 3\,O_2\uparrow$$

4. *Double replacement,* or if the reaction takes place between ions in solution, *direct combination of a cation with an anion.*

(a) Acid + base = salt + water (neutralization)

$$H^+ + Cl^- + Na^+ + OH^- = Na^+ + Cl^- + H_2O$$

This illustrates a characteristic property of an acid and a base.

(b) Salt + acid = salt + acid

$$2\,\mathbf{KNO_3} + H_2SO_4\ (\text{heated}) = K_2SO_4 + 2\,HNO_3\uparrow$$

This has already been used as a method for preparing an acid. It illustrates a chemical property of an acid and a chemical property of a salt.

(c) Salt + base = salt + base

$$Ni^{++} + 2\,Cl^- + 2\,Na^+ + 2\,OH^- = 2\,Na^+ + 2\,Cl^- + \mathbf{Ni(OH)_2}$$

$$2\,K^+ + SO_4^{--} + Ba^{++} + 2\,OH^- = \mathbf{BaSO_4} + 2\,K^+ + 2\,OH^-$$

One of the products, either the base or the salt, must be insoluble so that it can be filtered off. The soluble product can then be recovered by evaporating the solution to dryness.

(d) Salt + salt = salt + salt

$$Ag^+ + NO_3^- + Na^+ + Cl^- = \mathbf{AgCl} + Na^+ + NO_3^-$$

As in the previous method, one of the products must be insoluble. A reaction of the type

$$K^+ + NO_3^- + Na^+ + Cl^- \rightleftarrows K^+ + Cl^- + Na^+ + NO_3^-$$

will yield a mixture of salts when evaporated to dryness.

5. *Specific oxidation-reduction reactions* that will be discussed when they arise.

13.13 When will a reaction occur between ions in solution? The discussion of the properties of acids and bases and the preparation of acids, bases, and salts in Sections 13.1, 13.4, 13.5, 13.7, and 13.12 raises a major question: How can we know whether or not a reaction will take place when two or more electrolytes are brought together in solution, and if they do react, what the products will be?

In arriving at an answer we should first note that nearly all reactions in solution fall in one of three classes:

1. *Simple replacement of an ion or element by a more active element.* (As noted in Section 4.7, replacement reactions are oxidation-reduction reactions. However, because of their unique character they are not at this time placed in the same class with other oxidation-reduction reactions referred to in 3 below.)

$$\mathbf{Zn} + Cu^{++} = Zn^{++} + \mathbf{Cu}$$

$$\mathbf{Mg} + 2\,H^+ = Mg^{++} + H_2\uparrow$$

$$2\,\mathbf{K} + 2\,H_2O = 2\,K^+ + 2\,OH^- + H_2\uparrow$$

$$Cl_2 + 2\,Br^- = 2\,Cl^- + Br_2$$

2. *Direct combination of a cation with an anion*

$$H^+ + OH^- = H_2O$$

$$Ag^+ + Cl^- = \mathbf{AgCl}$$

$$CO_3^{--} + 2\,H^+ = H_2O + CO_2\uparrow$$

3. *Oxidation of a constituent of one ion or molecule by another ion or molecule.*

In looking back over the three classes of reactions as listed above, we find that the question of when a replacement reaction will take place has been pretty well answered in Chapter 4 and in Section 13.12. The oxidation-reduction reactions involving ions will be discussed later; at that time we shall find that it will be comparatively easy to decide whether or not a certain ion will oxidize another. The only problem at the moment then, is knowing when an anion will combine with a cation. It can be stated that, *as a general rule, whenever two electrolytes are brought together in solution or under such conditions that a solution can form, the positive ion (cation) of one electrolyte will always tend to combine with the negative ion (anion) of the other to form a compound;* the chemical formula of the compound will be determined by the valences of the combining ions. However, this combination of oppositely charged ions to form a compound *will actually take place only if:*

1. *The resulting compound is insoluble or decomposes to give an insoluble compound.* The common insoluble compounds are listed in Tables 11.2 and 11.3, page 222 and 223.

2. *The resulting compound is a weak electrolyte, and hence is only slightly ionized.*

$$H^+ + OH^- = H_2O$$
$$NH_4^+ + OH^- = NH_3 + H_2O$$
$$3\,H^+ + PO_4^{---} = H_3PO_4$$

The common weak electrolytes are listed in Section 12.4, page 241. (We shall learn, in Chapter 14, that stable complex ions, which are often formed, are partly dissociated, and hence behave like weak electrolytes. Their formation will cause a reaction to take place.)

Applying the above rules we can conclude:

(a) A reaction will take place when Na_2SO_4 and $BaCl_2$ are brought together in solution because $BaSO_4$ is insoluble.

$$Ba^{++} + SO_4^{--} = \mathbf{BaSO_4}$$

(b) No reaction will take place when solutions of KNO_3 and $Ca(OH)_2$ are brought together, because no insoluble compounds or weak electrolytes are formed.

(c) A reaction will take place when solid $Mg(OH)_2$ is treated with a solution of HCl, because the weak electrolyte H_2O is formed.

$$\mathbf{Mg(OH)_2} \rightleftarrows Mg^{++} + 2\,OH^-$$
$$2\,OH^- + 2\,H^+ = 2\,H_2O$$

(d) A reaction will take place when a solution of Na_2CO_3 is treated with a solution of $CaCl_2$, because $CaCO_3$ is insoluble.

$$CO_3^{--} + Ca^{++} = \mathbf{CaCO_3}$$

(e) A reaction will take place when a solution of Na_2CO_3 is treated with a strong acid because CO_2 gas is insoluble and H_2O is a weak electrolyte.

$$CO_3^{--} + 2\ H^+ = H_2O + CO_2\uparrow$$

13.14 Equivalence in single-replacement and double-replacement reactions

A. *Equivalent Weights of Elements.* We learned in Section 4.11 that

1. *A specific quantity of one substance is said to be equivalent to a specific quantity of another substance, chemically, when it will combine with it, replace it, or be replaced by it.* Thus 1 gram-atom of sodium is equivalent to 1 gram-atom of hydrogen; this is shown by the formula of the compound, NaH, in which 1 gram-atom of sodium is combined with 1 gram-atom of hydrogen, and by the molecular equation, $2\ Na + 2\ HCl = 2\ NaCl + H_2$, in which 1 gram-atom of sodium replaces 1 gram-atom of hydrogen.

2. *The gram-equivalent weight of an element is the weight of that element that will combine with or replace 1 gram-atom of hydrogen or its equivalent.* Hydrogen is selected as a reference standard, and all other elements are compared with it. Because 1 gram-atom of oxygen combines with 2 gram-atoms of hydrogen in H_2O, it follows that $\frac{1}{2}$ gram-atom (8 g) of oxygen is equivalent to 1 gram-atom (1.008 g) of hydrogen. Likewise, because 1 gram-atom of chlorine combines with 1 gram-atom of hydrogen in HCl, it follows that 1 gram-atom (35.46 g) of chlorine is equivalent to 1 gram-atom (1.008 g) of hydrogen. In accordance with these facts, the term *gram-equivalent weight* is defined, more broadly, as the weight of an element which will combine with or replace 1 gram-atom (1.008 g) of hydrogen, $\frac{1}{2}$ gram-atom (8.00 g) of oxygen, or 1 gram-atom (35.46 g) of chlorine.

3. When a binary compound takes part in a single-replacement or double-replacement reaction (see 13.1–5 and 13.1–6), *the equivalent weight of an element in the compound is equal to its atomic weight divided by its oxidation number (valence) in that compound.* The valence (oxidation number) of hydrogen is 1. If 1 atom of an element combines with 1 atom of hydrogen, the oxidation number (valence) of that element must be 1. If 1 atom of an element combines with 2 atoms of hydrogen, the oxidation number (valence) of that element must be 2. When 1 gram-atom of an element combines with 2 gram-atoms of hydrogen, as is the case when the oxidation number of the element is 2, the equivalent weight of that element is one-half its atomic weight. From these three generalizations we can conclude that

4. *A certain fraction of the equivalent weight of one element will always combine with, replace, or be replaced by that same fraction of the equivalent weight of any other element.* One gram-equivalent weight (23.0 g) of sodium will combine with

1 gram-equivalent weight (35.46 g) of chlorine to form the compound NaCl; $\frac{1}{2}$ gram-equivalent weight of sodium will therefore combine with $\frac{1}{2}$ gram-equivalent weight of chlorine, 0.1 gram-equivalent weight of sodium will combine with 0.1 gram-equivalent weight of chlorine, and 0.002 gram-equivalent weight of sodium will combine with 0.002 gram-equivalent weight of chlorine. From the balanced molecular equation

$$Ca + 2\ HCl = CaCl_2 + H_2$$

we conclude that the oxidation number (valence) of calcium is 2 and that its gram-equivalent weight is one-half its gram-atomic weight, or 20.04 g. Two gram-equivalent weights (40.08 g) of calcium will liberate 2 gram-equivalent weights (2.016 g) of hydrogen; 0.1 gram-equivalent weight (2.004 g) of calcium will liberate 0.1 gram-equivalent weight of hydrogen.

B. *Equivalent Weights of Compounds.* If we recall the equations that we have studied to date, we will find that the concept of equivalence can be carried over to compounds. From the equation

$$H_2 + Cl_2 = 2\ HCl$$

we see that 2 gram-atoms of H produce 2 moles of HCl. That is, 1 gram-atom of H will yield 1 mole of HCl. We can say therefore that 1 mole of HCl is equivalent to 1 gram-atom of H, and that the equivalent weight of HCl is 36.5 (its molecular weight). Now if we use HCl as the yardstick, the standard by which we compare other compounds, we can see from the equation

$$NaOH + HCl = NaCl + H_2O$$

that 1 mole of HCl is equivalent to 1 mole of NaOH. Therefore the equivalent weight of NaOH is its formula weight. If we consider the equation

$$2\ HCl + Ca(OH)_2 = CaCl_2 + 2\ H_2O$$

we can see that 1 mole of $Ca(OH)_2$ is equivalent to 2 moles of HCl. In other words, $\frac{1}{2}$ mole of $Ca(OH)_2$ is equivalent to 1 mole of HCl. That is, the equivalent weight of $Ca(OH)_2$ is one-half its formula weight. The reason for this last fact is that the valence of the calcium ion is 2. So here we see valence coming into the picture again and we conclude that the equivalent weight of a compound, when it takes part in a simple double replacement reaction, is its formula weight divided by the valence of its ions. This conclusion is verified when we find that, according to the reaction represented by the equation

$$Al(OH)_3 + 3\ HCl = AlCl_3 + 3\ H_2O$$

the equivalent weight of $Al(OH)_3$ is one-third its formula weight. From the reaction

$$3\ NaOH + H_3PO_4 = Na_3PO_4 + 3\ H_2O$$

we can conclude that the equivalent weight of H_3PO_4 is one-third its formula weight. So we can generalize and state that *the equivalent weight of a compound, when it takes part in ordinary double replacement reactions, is its formula weight*

divided by the total valence of its positive or negative ions. In applying this rule we must know what ions are actually involved in the course of the over-all reaction. The salt $AlCl_3$ yields Al^{+++} and Cl^- ions; the total positive valence is 3 and the total negative is also 3; therefore its equivalent weight is one-third its formula weight. The salt $Fe_2(SO_4)_3$ gives Fe^{+++} and SO_4^{--} ions; the total positive valence (or negative valence) is 6; therefore its equivalent weight is one-sixth its formula weight. The acid H_3AsO_3 yields H^+ and $H_2AsO_3^-$ ions; it does not yield H^+ and AsO_3^{---} ions. Therefore it is a monoprotic acid, and its equivalent weight, when it takes part in a double replacement reaction, is equal to its formula weight.

C. *Equivalence in Reactions.* If we examine the equations just given we will arrive at the important conclusion that *in any single-replacement or double-replacement reaction the number of gram-equivalents of one reactant or product is exactly equal to the number of gram-equivalents of any other reactant or product.* Thus in the reaction

$$NaOH + HCl = NaCl + H_2O$$

1 gram-equivalent (1 mole) of NaOH reacts with 1 gram-equivalent (1 mole) of HCl to yield 1 gram-equivalent (1 mole) of NaCl and 1 gram-equivalent (1 mole) of H_2O. If 0.1 gram-equivalent of NaOH had been used, 0.1 gram-equivalent of HCl would have reacted and 0.1 gram-equivalent each of NaCl and H_2O would have been formed.

In the reaction

$$2\,HCl + Ca(OH)_2 = CaCl_2 + 2\,H_2O$$

2 gram-equivalent weights (2 moles) of HCl react with 2 gram-equivalent weights (1 mole) of $Ca(OH)_2$ to form 2 gram-equivalent weights (1 mole) of $CaCl_2$ and 2 gram-equivalent weights (2 moles) of H_2O.

In the reaction

$$Al(OH)_3 + 3\,HCl = AlCl_3 + 3\,H_2O$$

3 gram-equivalents (3 moles) of HCl react with 3 gram-equivalents (1 mole) of $Al(OH)_3$ to form 3 gram-equivalents (1 mole) of $AlCl_3$ and 3 gram-equivalents (3 moles) of H_2O.

In the reaction

$$6\,NaOH + Fe_2(SO_4)_3 = 3\,Na_2SO_4 + 2\,Fe(OH)_3$$

6 gram-equivalents (6 moles) of NaOH react with 6 gram-equivalents (1 mole) of $Fe_2(SO_4)_3$ to form 6 gram-equivalents (3 moles) of Na_2SO_4 and 6 gram-equivalents (2 moles) of $Fe(OH)_3$.

In the reaction

$$Zn + 2\,HCl = ZnCl_2 + H_2$$

2 gram-equivalents (1 gram-atom) of Zn react with 2 gram-equivalents (2 moles) of HCl to form 2 gram-equivalents (1 mole) of $ZnCl_2$ and 2 gram-equivalents (1 mole or 2 gram-atoms) of hydrogen.

In the reaction

$$3\,Cl_2 + 2\,AlBr_3 = 3\,Br_2 + 2\,AlCl_3$$

6 gram-equivalents (3 moles or 6 gram-atoms) of chlorine react with 6 gram-equivalents (2 moles) of $AlBr_3$ to form 6 gram-equivalents (3 moles or 6 gram-atoms) of bromine and 6 gram-equivalents (2 moles) of $AlCl_3$.

D. *Equivalent Weights of Ions.* What has been said about equivalent weights of elements and compounds applies equally well to ions. The gram-equivalent weight of any ion is equal to its gram-ion weight divided by its valence. Thus the gram-equivalent weight of the Ba^{++} ion is one-half the gram atomic weight of Ba, and the gram-equivalent weight of the SO_4^{--} ion is one-half the gram-ion weight of the SO_4^{--} ion. The gram-equivalent weight of the PO_4^{---} ion is one-third its gram-ion weight, while the gram-equivalent weight of the NO_3^- ion is equal to its gram-ion weight. The gram-ion weight is, it will be recalled, equal to the sum of the gram-atomic weights of the constituent atoms. Thus the gram-ion weight of the SO_4^{--} ion is 96 g (1 S = 32 g, and 4 O = 64 g), while for the NO_3^- ion it is 62 g (1 *N* = 14 g and 3 O = 48 g).

In the reaction

$$Ba^{++} + SO_4^{--} = \mathbf{BaSO_4}$$

2 gram-equivalent weights (1 gram-ion) of Ba^{++} react with 2 gram-equivalent weights (1 gram-ion) of SO_4^{--} to form 2 gram-equivalent weights (1 mole) of $BaSO_4$.

In the reaction

$$CO_3^{--} + 2\,H^+ = H_2CO_3\,(H_2O + CO_2)$$

2 gram-equivalents (1 gram-ion) of CO_3^{--} react with 2 gram-equivalents (2 gram-ions) of H^+ to form 2 gram-equivalents (1 mole) of H_2CO_3.

In the reaction

$$6\,K + 2\,H_3PO_4 = 6\,K^+ + 2\,PO_4^{---} + 3\,H_2$$

6 gram-equivalents (6 gram-atoms) of K react with 6 gram-equivalents (2 moles) of H_3PO_4 to form 6 gram-equivalents (6 gram-ions) of K^+, 6 gram-equivalents (2 gram ions) of PO_4^{---}, and 6 gram-equivalents (3 moles or 6 gram-atoms) of hydrogen.

E. *Calculations Based on Equivalence.* The fact that, in any replacement or double-replacement reaction, the number of gram-equivalents of each reactant and product is exactly equal, can be used in making calculations based on the stoichiometry of the reaction. To illustrate suppose we want to solve the problem, How many grams of NaOH will be required to react with a solution containing 2 gram-equivalents of HCl?

We first note that

number of gram-equivalents of NaOH = number of gram-equivalents of HCl

Therefore 2 gram-equivalents of NaOH will be required. The gram-equivalent weight of NaOH is equal to its gram-formula weight. Therefore 1 gram-equivalent of NaOH is 40 g.

2 gram-equivalents of NaOH × 40 g of NaOH per gram-equivalent
= 80 g of NaOH

For the problem, How many gram-equivalents of $Ca(OH)_2$ will be required to neutralize a solution containing 20 g of H_3PO_4? we note that

number of gram-equivalents of $Ca(OH)_2$
= number of gram-equivalents of H_3PO_4

The equivalent weight of H_3PO_4 is one-third its formula weight, that is, $\frac{1}{3} \times 98$, or 32.67. The number of gram-equivalents of H_3PO_4 will then be 20 g ÷ 32.67 g per gram-equivalent, or 0.61 gram-equivalent. Therefore 0.61 gram-equivalent of $Ca(OH)_2$ will be required. It should be noted that it is common practice to use the term *equivalents* rather than gram-equivalents when solving problems of this type; in such a case it is understood that equivalents means gram-equivalents.

For the problem, How many grams of AgCl will be formed by addition of excess Cl^- to a solution containing 0.200 equivalents of Ag^+? we note that

equivalents of AgCl = equivalents of Ag^+

Therefore 0.200 equivalent of AgCl will be formed. The equivalent weight of AgCl is equal to its formula weight, 143.3. The number of grams of AgCl will then be 0.2 equivalent × 143.3 g per equivalent = 28.7 g.

F. *Equivalence Applied to Reactions in Solution.* Since 1 gram-equivalent weight of one substance will react with 1 gram-equivalent weight of another substance, it follows that a liter of solution which contains exactly 1 gram-equivalent of HCl will just neutralize a liter of solution that contains exactly 1 gram-equivalent of NaOH; 100 ml of the first solution will neutralize 100 ml of the second solution; 1 ml of the first solution will neutralize 1 ml of the second solution. What this means, very simply, is that a specific number of equivalents of HCl will react with an exactly equal number of equivalents of NaOH. It follows therefore that 1 l of HCl solution that contains 1 gram-equivalent of HCl per liter will neutralize 500 ml of an NaOH solution that contains 2 gram-equivalents of NaOH per liter. One liter of an HCl solution that contains 1 gram-equivalent of HCl per liter will neutralize 5 l of NaOH solution that contain 0.2 gram-equivalent of NaOH per liter. We see from these examples that:

(1) number of milliliters of HCl solution × equivalents of HCl per 1000 ml = the number of milliliters of NaOH solution that this HCl will neutralize × equivalents of NaOH per 1000 ml

In the above expression "equivalents of HCl per 1000 ml" denotes the concentration of the solution in equivalents per liter; by definition this is called the *normality* of the solution. To be more specific, *the normality of the solution represents the number of gram-equivalents of solute per liter of solution.* Thus a liter of normal (1 *N*) HCl contains 1 gram-equivalent (36.5 g) of HCl, a liter of 0.2 *N* HCl contains 0.2 gram-equivalent (7.3 g) of HCl, while the concentration of 0.4 *N* HCl is 0.4 equivalent of HCl per liter of solution. We can therefore

substitute "normality of HCl (or NaOH)" for "equivalents of HCl (or NaOH) per 1000 ml" in equation (1). This gives us

(2) milliliters of HCl solution × normality of HCl solution = milliliters of NaOH solution × normality of NaOH solution

The general formula covering any replacement or double replacement reaction in which a substance A reacts with or yields a substance B is

(3) milliliters of solution of A × normality of solution of A = milliliters of solution of B × normality of solution of B

It should be noted that in equation (1) the term "equivalents of HCl per 1000 ml" can be expressed in mathematical form as

$$\frac{\text{equivalents of HCl}}{1000 \text{ ml}}$$

Using the mathematical form, we obtain the expression

$$\text{(4)} \qquad \text{milliliters of HCl} \times \frac{\text{equivalents of HCl}}{1000 \text{ ml of HCl}} = \text{milliliters of NaOH} \times \frac{\text{equivalents of NaOH}}{1000 \text{ ml of NaOH}}$$

But

$$\text{milliliters of HCl} \times \frac{\text{equivalents of HCl}}{1000 \text{ ml of HCl}} = \text{total equivalents of HCl}$$

and

$$\text{milliliters of NaOH} \times \frac{\text{equivalents of NaOH}}{1000 \text{ ml of NaOH}} = \text{total equivalents of NaOH}$$

Equation (4) expresses, therefore, the fact that

$$\text{total equivalents of HCl} = \text{total equivalents of NaOH}$$

It follows from what has just been stated that the number of equivalents of base in a quantity of solution can be calculated by measuring the exact number of milliliters of acid of known normality that are required to neutralize it. To illustrate, suppose exactly 100 ml of 1 *N* HCl were required to neutralize the NaOH solution in a beaker. 1 *N* HCl contains 1 equivalent of HCl per 1000 ml. The number of equivalents of HCl that were required will be

$$100 \text{ ml of HCl} \times \frac{1 \text{ equivalent of HCl}}{1000 \text{ ml of HCl}} = 0.1 \text{ equivalent of HCl}$$

That means that 0.1 equivalent of NaOH was present in the solution in the beaker.

Solutions of definite known concentration (normality in this case) are referred to as *standard solutions*. The process whereby such solutions are used for the experimental determination of the concentration of another solution or the quantity of some other substance is called *titration*. Experiments illustrating titration will be performed in the laboratory (see Figure 13.1).

To illustrate calculations involved in titration with standard solution consider the problem: A total of 120 ml of 0.50 N H_2SO_4 were required to neutralize 400 ml of potassium hydroxide solution. Calculate the normality of the KOH solution.

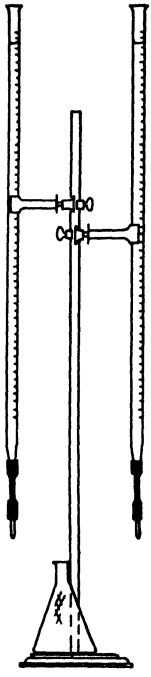


Figure 13.1. Burets for use in titration. A definite volume of the solution to be analyzed (a base in this instance) is transferred from one buret to the flask. A small amount of indicator solution is then added to the flask. Standard acid is added from the second buret until the behavior of the indicator shows that the base has been exactly neutralized. From the volume of standard acid used the concentration of the base in the solution can be calculated.

Finding the normality of the KOH means finding the number of equivalents of KOH per liter of solution.

equivalents of H_2SO_4 = equivalents of KOH

$$120 \text{ ml of } H_2SO_4 \times \frac{0.50 \text{ equiv. of } H_2SO_4}{1000 \text{ ml of } H_2SO_4} = 400 \text{ ml of KOH} \times \frac{X \text{ equiv. of KOH}}{1000 \text{ ml of KOH}}$$

Solving the expression, we find that

$$X = \frac{120 \times 0.50 \text{ equiv.}}{400} = 0.15 \text{ equivalent of KOH}$$

Therefore the KOH solution is 0.15 N.

Note that in the original expression given above, 1000 ml will cancel from the denominator on both sides of the equation. This gives rise to the simplified expression

$$120 \text{ ml of } H_2SO_4 \times 0.50 \text{ equiv. of } H_2SO_4 = 400 \text{ ml of KOH} \times X \text{ equiv. of KOH}$$

This latter expression illustrates the fact that in any reaction between solutions of two reactants A and B,

$$\text{milliliters of A} \times \text{normality of A} = \text{milliliters of B} \times \text{normality of B}$$

Using this expression, we can calculate the problem given above by stating, simply, that

$$120 \text{ ml of } H_2SO_4 \times 0.5\ N = 400 \text{ ml of KOH} \times X\ N$$

$$X = \frac{120 \times 0.5}{400} = 0.15\ N$$

Titration with standard solutions plays a prominent role in many types of chemical analysis.

13.15 Natural waters. Natural water as it is found in wells, springs, rivers, lakes, and oceans is a solution containing varying amounts of a variety of solutes. These solutes fall, roughly, into three classes:

1. *Dissolved gases.* This is largely air, with some CO_2.

2. *Organic matter.* This includes all bacteria and other microorganisms, and various substances derived from the decay of animal and vegetable matter. Because this organic matter is readily oxidized by the oxygen in the air, the amount present in most natural water is very small.

3. *Mineral matter.* This includes such salts as the chlorides, sulfates, carbonates, and hydrogen carbonates of calcium, magnesium, sodium, potassium, and iron. Their total concentrations range all the way from about 23% in Great Salt Lake to about 3.6% in sea water to as little as 0.001% in some lakes and wells. The salts are dissolved from the soil and rocks with which the water comes in contact as it seeps down through the earth's outer crust or flows over its surface; since they are strong electrolytes they will exist in solution in the ionic form.

When ordinary soap ($NaC_{17}H_{35}COO$, sodium stearate) is added to water containing such heavy metal ions as Ca^{++}, Mg^{++}, and Fe^{+++}, sudsing does not take place unless large quantities of soap are used; instead, a curd (precipitate) of insoluble $Ca(C_{17}H_{35}COO)_2$, $Mg(C_{17}H_{35}COO)_2$, and $Fe(C_{17}H_{35}COO)_3$ forms. Water which contains heavy metal ions, and as a result shows this behavior, is said to be *hard;* the greater the concentration of the Ca^{++}, Mg^{++}, and Fe^{+++} (and other heavy metal cations), the harder the water. This concentration is generally expressed in units of *parts per million* or *grains per gallon.*

Parts per million means *parts by weight of* $CaCO_3$ *or its equivalent per million parts by weight of water. Grains per gallon* means *grains of* $CaCO_3$ *or its equivalent per gallon of water.*

As has already been indicated, hardness in water is due to the presence of Ca^{++}, Mg^{++}, Fe^{+++}, and other heavy metal ions. It is not due to the presence of $CaCO_3$. Why then is hardness expressed in units of parts by weight of $CaCO_3$ or its equivalent? The reason for the choice of $CaCO_3$ is this: calcium ions are the chief source of hardness in water. If the hard water contains HCO_3^- ions as well as Ca^{++} ions, boiling causes precipitation of $CaCO_3$ in accordance with the net equation

$$Ca^{++} + 2\,HCO_3^- = \mathbf{CaCO_3} + H_2O + CO_2\uparrow$$

The quantity of $CaCO_3$ that precipitated in boiling was historically the first measure of the amount of hardness in water. Its choice as a reference standard was therefore a natural one; actually it is an excellent one.

One gram-ion of Ca^{++} ions will yield 1 mole of $CaCO_3$,

$$Ca^{++} + CO_3^{--} = \mathbf{CaCO_3}$$

That means that 1 gram-ion of Ca^{++} ions is *equivalent to* 1 mole (100 g) of $CaCO_3$. The Mg^{++} ion has the same valence as the Ca^{++} ion; therefore 1 gram-ion of

Mg^{++} is equivalent to 1 gram-ion of Ca^{++}. Since things equivalent to the same things, chemically, are equivalent to each other, 1 gram-ion of Mg^{++} is equivalent to 1 mole (100 g) of $CaCO_3$. In the same way, 1 gram-ion of any divalent ion (Zn^{++}, Cu^{++}, Mn^{++}, Ba^{++}) is equivalent to 1 mole (100 g) of $CaCO_3$, 1 gram-ion of any monovalent ion (Ag^+) is equivalent to $\frac{1}{2}$ mole (50 g) of $CaCO_3$, and 1 gram-ion of a trivalent cation (Fe^{+++}, Al^{+++}, Cr^{+++}) is equivalent to $\frac{3}{2}$ moles (150 g) of $CaCO_3$. If 1 million grams of water contained 1 gram-ion of Ca^{++} ions (associated with Cl^-, SO_4^{--}, and HCO_3^- ions) as the only solute causing hardness, its hardness would be 100 parts per million (100 ppm); the 1 gram-ion of Ca^{++} is equivalent to 100 g of $CaCO_3$. If 1 million grams of water contained 1 gram-ion of Mg^{++} ions as the only solute causing hardness, its hardness would also be 100 ppm; the 1 gram-ion of Mg^{++} is equivalent to 100 g of $CaCO_3$. If 1 million grams of water contained 1.5 gram-ions of Mg^{++}, 1.2 gram-ions of Ca^{++}, and 0.5 gram-ion of Fe^{+++} as the only solute ions causing hardness, the total hardness would be 345 parts per million; $1.5 \times 100 = 150$ parts due to the Mg^{++} ions, $1.2 \times 100 = 120$ parts due to the Ca^{++}, and $0.5 \times 150 = 75$ parts due to the Fe^{+++}. The fact that $CaCO_3$ happens to have a molecular weight of 100 makes these calculations very simple.

One gallon of water weighs 58,823 grains. Therefore a hardness of 1 grain per gallon would be the same as 1 grain per 58,823 grains. Now 1 is to 58,823 as 17 is to 1,000,000. Therefore a hardness of 1 grain per gallon is the same as 17 parts per million. If hardness is given in grains per gallon and we want to convert it to units of parts per million we multiply by 17. If it is given in parts per million and we want to change it to grains per gallon, we divide by 17.

It is obvious from what has been stated above, that to determine the hardness of water, we need only determine the number of gram-ions of heavy metal ions in 1 million grams. Up until a few years ago this was generally done by titrating a small sample of the water with standard soap solution. At present organic compounds of a class known as *versenates* are widely used as titrating agents. The *equivalence point* (the point at which the titrating agent has reacted with all the heavy metal ions) is shown by the change in color of an indicator in the same way that the complete neutralization of a base by an acid is shown by the change in color of litmus, methyl orange, or phenolphthalein.

Hardness that can be removed from water by boiling is called *temporary hardness*. It is due to the presence of HCO_3^- ions associated with Ca^{++} and Mg^{++} ions. Its removal is evidenced by precipitation of $CaCO_3$, and sometimes $MgCO_3$, as a consequence of the reactions

$$Ca^{++} + 2\,HCO_3^- = \mathbf{CaCO_3} + H_2O + CO_2\uparrow$$
$$Mg^{++} + 2\,HCO_3^- = \mathbf{MgCO_3} + H_2O + CO_2\uparrow$$

Hardness that cannot be removed by boiling is called *permanent* hardness. It is caused largely by the presence of chlorides and sulfates of calcium and magnesium.

If hard water is evaporated to dryness the solid residue that remains

is largely a mixture of $CaCO_3$, $CaSO_4$, $CaCl_2$, $MgCO_3$, $MgCl_2$, $MgSO_4$, and NaCl.

The mineral salts and dissolved air and carbon dioxide that are present in water give it its characteristic desirable taste. If they were absent the taste would be very flat. Too much hardness in water, however, makes it undesirable for washing and for use in steam boilers and for other industrial uses. Hard water consumes a lot of soap because the heavy metal ions must be precipitated by the soap before a lather will form. It will yield a deposit of $CaCO_3$, $CaSO_4$, and other salts in steam boilers; this is referred to as *boiler scale*, and its formation results in wastage of fuel and boiler collapse because of poor heat transfer through the scale.

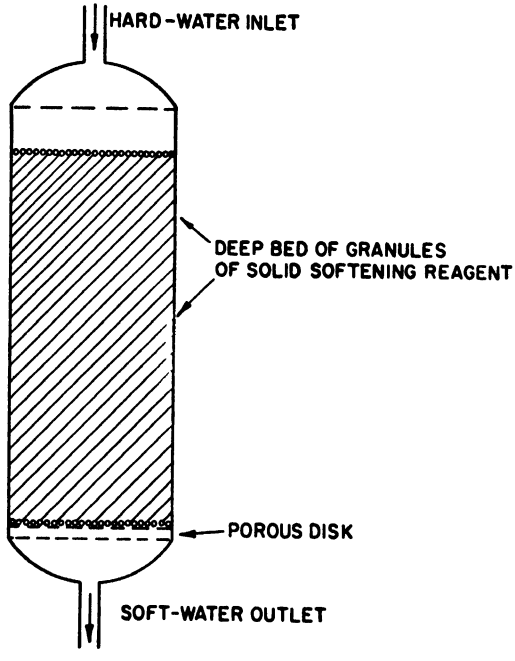


Figure 13.2. Household water softening unit.

Water is *softened* (hardness removed) by treating with a chemical substance which forms a precipitate with the heavy metal ions. There are a number of such substances in use, one of them being a complex sodium aluminum silicate known as a *zeolite*. The hard water is allowed to flow through a drum filled with the solid zeolite (see Figure 13.2). The following reaction, in which the zeolite is represented by the formula NaZ, takes place.

$$Ca^{++} + 2\,NaZ = CaZ_2 + 2\,Na^+$$
$$Mg^{++} + 2\,NaZ = MgZ_2 + 2\,Na^+$$

It should be noted that the Ca^{++} and Mg^{++} ions in the hard water are replaced by an exactly equivalent amount of Na^+ ions. These Na^+ ions are not undesirable since they do not interfere with the cleansing action of soap or cause formation of curd. The spent zeolite can be regenerated by flushing it out with a solution of sodium chloride. The exact reverse of the above reactions takes place.

$$2\,Na^+ + CaZ_2\ (MgZ_2) = Ca^{++}\ (Mg^{++}) + 2\,NaZ$$

It should be noted that detergents are available that form strong suds and no curd with hard water. They do not react with the heavy metal ions as does ordinary soap.

Harmful bacteria in water are commonly destroyed by treatment with chlorine. Suspended material is removed by filtration through sand and gravel filter beds (see Figure 13.3). Treatment of the water, before

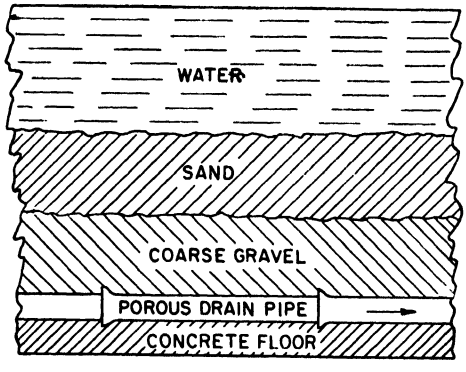


Figure 13.3. Cross section of a water filter bed.

filtration, with chemicals that produce gelatinous precipitates [$Al(OH)_3$ and $Fe(OH)_3$] aids in the removal of various impurities.

Questions and Problems

1. Define or describe, and illustrate each of the following: electrolyte; acid; base; salt; hydronium ion; anion; cation; proton donor; proton acceptor; neutralization; molecular equation; detailed ionic equation; net equation; predominant reacting species; stoichiometry; strong acid; weak acid; 1 gram-equivalent weight of solute; binary acid; ternary acid; volatile acid; nonvolatile acid; monohydrogen acid; monoprotic acid; dibasic acid; polybasic acid; polyprotic acid; *ortho* acid; *meta*

acid; acid anhydride; replacement reaction; double-replacement reaction; double-decomposition reaction; hydrolysis; strong base; weak base; alkali; alkali metal; alkali metal group; alkaline earth metal; alkaline earth group; monoacidic base; polyacidic base; normal salt; acid salt; basic salt; equivalent weight; gram-equivalent weight; gram-equivalent; natural water; hard water; soft water; hardness of water; parts per million; grains per gallon; temporary hardness; permanent hardness.

2. List all the properties of a solution of HCl in water which identify it as an acid.

3. Describe the experimental methods that can be used to show that HCl is a stronger acid than $HC_2H_3O_2$. Account for the results that are observed in each test in terms of the per cent ionization of each acid.

4. List the methods that can be used for preparing acids and give two equations to illustrate each method.

5. Give the formula of the anhydride of each of the following ternary acids: $HClO_3$, HNO_2, H_3PO_3, H_3PO_4, H_2CrO_4, $H_2Cr_2O_7$, $HClO_2$, HBrO.

6. Give the formula of the ternary acid that would be formed when each of the following is dissolved in water: SO_2, SO_3, N_2O_5, Cl_2O_7, As_2O_3, Cl_2O.

7. List all the properties of a solution of NaOH in water which identify it as a base.

8. How do you account for the fact that the solutions of the hydroxides of strongly electropositive elements are basic, while the solutions of the hydroxides of electronegative elements are acidic?

9. How can you determine the relative strengths of two bases? Account for the results that are observed.

10. List the methods that can be used for formation of bases and basic oxides and give one equation to illustrate each method.

11. List the methods that can be used for preparation of normal salts and give two equations to illustrate each method.

12. Into what three broad classes or types do nearly all reactions involving solutions of electrolytes fall? Give two examples to illustrate each of two of these classes.

13. List the conditions under which a cation and an anion in solution will react with each other. Illustrate each.

14. What is the equivalent weight of each of the following compounds when it takes part in a replacement or double replacement

reaction: HCl, H_2SO_4, H_3PO_4, $Cu(OH)_2$, KOH, $Al(OH)_3$, $NaCl$, $FeCl_3$, $CuSO_4$, $NiCl_2$, $Cr_2(SO_4)_3$?

15. What is the equivalent weight of each of the following ions when it takes part in a double replacement reaction: Cl^-, NO_3^-, SO_3^{--}, PO_4^{---}, OH^-, $Cr_2O_7^{--}$, Fe^{+++}, Cu^{++}, K^+?

16. Write net equations for the reactions that take place when each of the following sets of reactants are brought together in water solution.

(a) A strong base and a strong acid.
(b) A weak base and a weak acid.
(c) A weak soluble base and a strong acid.
(d) A strong base and a weak acid.
(e) A strong acid and a soluble metal carbonate.
(f) A strong acid and water-insoluble $CaCO_3$.
(g) A weak acid and a solution of Na_2CO_3.
(h) An insoluble base and a strong acid.
(i) Insoluble $Mg(OH)_2$ and acetic acid.
(j) An active metal and a strong acid.
(k) An active metal and a weak acid.
(l) A group IA metal and cold water.
(m) P_4O_{10} and water.
(n) KOH and $FeCl_3$.
(o) $AgNO_3$ and $NaCl$.
(p) $Ba(NO_3)_2$ and K_2SO_4
(q) $ZnCl_2$ and $NaNO_3$

17. Show, by net equations, all the ways that could be used for preparing KCl.

18. How could you demonstrate that phosphorus is a nonmetal? That calcium is a metal?

19. How could you demonstrate that $NaHSO_4$ is an acid salt?

20. In each of the following sets of 3 indicate which will evolve hydrogen gas at the fastest rate ("Ac" = $(C_2H_3O_2^-)$. In each part the volumes of the solutions are equal.

(a) 1 g Zn + 1 *M* HCl
1 g Zn + 1 *M* HOCl
1 g Zn + 1 *M* H_2SO_4

(b) 1 *M* HCl + 1 g Zn dust
1 *M* HCl + 1 g mossy Zn
1 *M* HCl + 1 g Zn sheet

(c) 1 g Zn + 1 *M* HAc + 0.5 *M* NaAc
1 g Zn + 1 *M* HAc + 1.0 *M* NaAc
1 g Zn + 1 *M* HAc + 2.0 *M* NaAc

(d) 0.10 *M* HCl + 1 g Zn at 25°C
0.15 *M* HCl + 1 g Zn at 25°C
0.10 *M* HCl + 1 g Zn at 35°C

21. How many grams of Na_2CO_3 will be required to react with a solution containing 0.300 equivalent of HCl?

22. How many cubic centimeters of a 24.0% solution of HCl whose density is 1.12 g/cc will be required to neutralize a solution containing 0.800 equivalent of KOH?

23. How many gram-equivalents of H_2SO_4 are there in a liter of a 77.0% solution of H_2SO_4 whose density is 1.70 g/cc?

24. How many grams of KOH will be required for the preparation of 500 ml of 0.400 *N* KOH?

25. What is the normality of a solution of NaOH which contains 6 g of NaOH per 300 ml of solution?

26. How many grams of KOH will be required to react with 250 ml of 0.80 *N* HCl?

27. How many milliliters of 0.25 *N* H_2SO_4 will be required to neutralize 15 g of pure NaOH?

28. Now many milliliters of 0.20 *N* HCl will be required to neutralize 150 ml of 0.15 *N* KOH?

29. A solution contained 2.00 g of KOH per liter. Calculate its normality.

30. How many milliliters of 0.250 *N* HCl will be required to neutralize 500 ml of solution containing 8.00 g of NaOH?

31. How many milliliters of 0.100 *N* H_2SO_4 will be required to neutralize 16.0 ml of a 10.0% solution of NaOH of density 1.12?

32. A 0.311 g sample of crude NaOH required 46.1 ml of 0.122 *N* H_2SO_4 to neutralize the NaOH in the sample. Calculate the per cent of NaOH in the crude material.

33. Fifteen milliliters of a 30% H_3PO_4 solution weigh 17.7 g. Find the molarity and the normality of the solution.

34. A measure of 2.4 g of an unknown acid is exactly neutralized by 30 ml of 0.40 *N* NaOH. Find the equivalent weight of the unknown acid.

35. A solution is 0.2 molar in Fe^{+++} ions. How many ml of 0.2 *N* KOH will be necessary to precipitate the Fe^{+++} ions from 400 ml of this solution?

36. What are the total hardness, temporary hardness, and permanent hardness of a sample of water, 1 million grams of which contain 0.04 gram-ion of HCO_3^-, 0.2 gram-ion of Ca^{++}, 0.1 gram-ion of Mg^{++}, 0.2 gram-ion of Cl^-, and 0.18 gram-ion of SO_4^{--}?

CHAPTER 14

Ionic Equilibria

We have already noted, in Sections 12.7 and 12.8, that ionization of all weak electrolytes is a reversible process which reaches a state of equilibrium. The ionization constant (Table 12.2) gives an index to the completeness of the ionization; weak electrolytes are sparingly ionized, and accordingly have low ionization constants. In this chapter certain ionization equilibria involving weak electrolytes will be given detailed consideration.

14.1 The ionization of water. Attention has already been called, in Section 12.8 and Table 12.2, to the fact that water is a very weak electrolyte. The equilibrium is represented by the equation

(1) $$H_2O \rightleftarrows H^+ + OH^-$$

and the ionization constant is represented by the expression

(2) $$K_i = \frac{[H^+] \times [OH^-]}{[H_2O]}$$

A liter of water (1000 g) will contain 55.5 moles of H_2O (1000 g ÷ 18 g/mole = 55.5555555 moles). Exact experimental measurements have shown that a liter of pure liquid H_2O at 25°C contains 1×10^{-7} gram-ion of H^+ ions and 1×10^{-7} gram-ion of OH^- ions. If we substitute these values in equations (1) and (2) we obtain

(3) $$\underset{55.5 - 1 \times 10^{-7}}{H_2O} \rightleftarrows \underset{1 \times 10^{-7}}{H^+} + \underset{1 \times 10^{-7}}{OH^-}$$

(4) $$K_i = \frac{(1 \times 10^{-7}) \times (1 \times 10^{-7})}{(55.5 - 1 \times 10^{-7})}$$

If H^+ ions (in the form of a strong acid, HCl, for example) are added to water, the equilibrium in reaction (3) will be shifted to the left in accordance with the common ion effect already discussed in Section 12.7. As a result of this shift the concentration of the un-ionized H_2O molecules will be increased, while the concentration of the OH^- ions will be decreased. Even if the concentration of H^+ ions added is so high that the concentration of OH^- ions is reduced practically to zero, the concentra-

tion of un-ionized H_2O molecules could increase only from 55.5555554 to 55.5555555; for all practical purposes that is no change at all. In other words, *the concentration of* H_2O *molecules in equilibrium with* H^+ *and* OH^- *ions is constant.* Therefore equation (4) becomes

$$(5) \qquad K_i = \frac{(1 \times 10^{-7})(1 \times 10^{-7})}{\text{constant whose value is } 55.5}$$

This constant whose value is 55.5 can be multiplied by the ionization constant K_i, to give a new constant which we will call the *ion product* for water; it is designated by the symbol K_{H_2O}. The numerical value of K_{H_2O} will therefore be $1 \times 10^{-7} \times 1 \times 10^{-7}$ or 1×10^{-14}. That is,

$$(6) \qquad K_{H_2O} = [H^+] \times [OH^-] = 1 \times 10^{-14}$$

As already noted in Chapter 12, $[H^+]$ and $[OH^-]$ mean concentration in gram-ions per liter of solution.

Equation (6) tells us that *the product of the* H^+ *ion and* OH^- *ion concentration in pure water or any water solution is always* 1×10^{-14}.

In pure water the H^+ and OH^- ion concentrations are the same; each is equal to 1×10^{-7} gram-ion per liter. Therefore pure water is neutral. If the H^+ ion concentration is greater than 1×10^{-7} gram-ion per liter, the OH^- ion concentration will be less than 1×10^{-7}; the solution will then be acidic, but the product of the two ion concentrations will still be 1×10^{-14}. The relation between $[H^+]$, $[OH^-]$, the ion product, and the condition of the solution is summarized in Table 14.1.

Equation (6) enables us to calculate

1. $[H^+]$ for any water solution whose $[OH^-]$ is known.
2. $[OH^-]$ for any water solution whose $[H^+]$ is known.
3. $[H^+]$ and $[OH^-]$ for solutions of acids or bases of known concentration and per cent ionization.

Thus the hydrogen ion concentration of a 0.01 molar solution of HCl which is 100% ionized is 1×10^{-2} gram-ion per liter. The OH^+ ion concentration can be calculated as follows:

$$[H^+] \times [OH^-] = 1 \times 10^{-14}$$

$$[OH^-] = \frac{1 \times 10^{-14}}{[H^+]} = \frac{1 \times 10^{-14}}{1 \times 10^{-2}} = 1 \times 10^{-12}$$

In making these calculations, the H^+ ions that are contributed by the H_2O are ignored because their concentration is so small (about 1×10^{-12} gram-ion per liter) compared with those contributed by the acid.

If the acid is extremely dilute, 10^{-8} molar for example, the quantity of hydrogen ions contributed by the water actually exceeds that contributed by the acid; in such a case, obviously, they cannot be ignored.

For 10^{-8} M HCl the total H^+ ion concentration will equal approximately $1 \times 10^{-7} + 1 \times 10^{-8}$, or 1.1×10^{-7} g ion/l, and the OH^- ion concentration will then be

$$\frac{1 \times 10^{-14}}{1.1 \times 10^{-7}} = 9 \times 10^{-8} \text{ gram-ion per liter}$$

14.2 pH. To avoid the use of the complex numbers, such as 1.1×10^{-7} or 6.34×10^{-12}, that are encountered when H^+ and OH^- ion concentrations are expressed in units of gram-ions per liter, the acidity or alkalinity of a solution is commonly expressed in *p*H *units. The* p*H of a solution is the logarithm of the reciprocal of the hydrogen ion concentration.* Expressed formulawise,

$$p\text{H} = \text{logarithm of } \frac{1}{[\text{H}^+]}$$

TABLE 14.1

IONIZATION OF WATER

$[H^+]$	$[OH^-]$	$[H^+] \times [OH^-]$	*Condition of solution*		*p*H
1×10^{0}	1×10^{-14}	1×10^{-14}	acidic	↑ Increasing acidity	0
1×10^{-1}	1×10^{-13}	1×10^{-14}	acidic		1
1×10^{-2}	1×10^{-12}	1×10^{-14}	acidic		2
1×10^{-3}	1×10^{-11}	1×10^{-14}	acidic		3
1×10^{-4}	1×10^{-10}	1×10^{-14}	acidic		4
1×10^{-5}	1×10^{-9}	1×10^{-14}	acidic		5
1×10^{-6}	1×10^{-8}	1×10^{-14}	acidic		6
1×10^{-7}	1×10^{-7}	1×10^{-14}	**neutral**		7
1×10^{-8}	1×10^{-6}	1×10^{-14}	alkaline	↓ Increasing alkalinity	8
1×10^{-9}	1×10^{-5}	1×10^{-14}	alkaline		9
1×10^{-10}	1×10^{-4}	1×10^{-14}	alkaline		10
1×10^{-11}	1×10^{-3}	1×10^{-14}	alkaline		11
1×10^{-12}	1×10^{-2}	1×10^{-14}	alkaline		12
1×10^{-13}	1×10^{-1}	1×10^{-14}	alkaline		13
1×10^{-14}	1×10^{0}	1×10^{-14}	alkaline		14

To illustrate, if the hydrogen ion concentration is 1×10^{-2} gram-ion per liter

$$p\text{H} = \log \frac{1}{10^{-2}} = \log 10^2 = 2$$

If the hydrogen ion concentration is 0.004 gram-ion per liter,

$$p\text{H} = \log \frac{1}{4 \times 10^{-3}} = \log \frac{10^3}{4} = \log 10^3 - \log 4$$
$$= 3 - 0.6 = 2.4$$

If the hydrogen ion concentration is 10^{-7} gram-ion per liter, as is the case with pure water, the *p*H is 7. Therefore a *p*H of 7 represents a

neutral solution. If the solution is acidic, the hydrogen ion concentration is greater than 10^{-7} gram-ion per liter, and the *p*H is less than 7. If the hydrogen ion concentration is less than 10^{-7} gram-ion per liter, the solution is alkaline (basic) and the *p*H is greater than 7. The relation between $[H^+]$, $[OH^-]$, *p*H, and the degree of acidity or alkalinity of a solution is summarized in Table 14.1.

14.3 Hydrolysis of normal salts. We learned in Section 13.12 that a normal salt can be prepared by neutralization of a base by an acid. One might expect, then, that the water solution of a normal salt would show a neutral reaction toward indicators. Such, however, is generally not the case. Thus, when the normal salt $NaC_2H_3O_2$ is dissolved in pure water, the resulting solution shows a pronounced alkaline reaction toward litmus. On the other hand a solution of pure NH_4Cl in water reacts distinctly acidic, while a solution of NaCl is neutral. If we extend this observation to solutions of other salts we find that Na_3PO_4, $NaBO_2$, Na_2CO_3, K_2SO_3, K_2CrO_4, $NaC_{17}H_{35}COO$, and Na_3AsO_4 all react alkaline, $FeCl_3$, $Pb(NO_3)_2$, $MgBr_2$, $Fe_2(SO_4)_3$, and $AlCl_3$ all react acidic, while KI, NaBr, $NaNO_3$, K_2SO_4, and NH_4F are neutral. If we examine the above results we note some very simple facts. If the salt contains the cation of a strong base and the anion of a weak acid, and can therefore be formed by the neutralization of a *strong base* by a *weaker acid*, its solution reacts *alkaline*. Thus Na_2CO_3, which reacts alkaline, contains the cation Na^+ and the anion $CO_3^=$, and may be looked upon as being derived from the strong base NaOH and the weak acid H_2CO_3. If the salt contains the cation of a weak base and the anion of a strong acid and can be looked upon as having been derived by the neutralization of a *strong acid* by a *weaker base* its solution reacts *acidic*. Thus $AlCl_3$, which reacts acidic, can be derived from the strong acid HCl and the weak base $Al(OH)_3$. If the salt is derived from an acid and a base of equal strength, either both strong, as in NaCl, or both equally weak, as in NH_4F, its solution will react neutral.

The simple relationships just noted will enable us to tell at a glance whether a solution of a salt will be acidic, alkaline, or neutral, provided we know the relative strengths of the various acids and bases. How can we account, in terms of reactions that actually take place, for the facts that we have noted?

We have already noted that pure water is ionized very slightly.

$$H_2O \rightleftarrows H^+ + OH^-$$

Because the concentration of H^+ ions is exactly the same as the concentration of OH^- ions, pure water is neutral. When $NaC_2H_3O_2$ is dissolved

in water it yields Na^+ ions and $C_2H_3O_2^-$ ions. The $C_2H_3O_2^-$ ions combine with the H^+ ions in the water equilibrium reaction and tie them up in the form of the weak acid $HC_2H_3O_2$. Since NaOH is a strong base and hence is 100% ionized, the Na^+ ions do not tie up OH^- ions. The result is that H^+ ions are removed from solution, while OH^- ions are not. The removal of H^+ ions shifts the H_2O ionization equilibrium to the right. This increases the concentration of OH^- ions. So not only is the concentration of H^+ ions reduced, but the concentration of OH^- ions is increased. The resulting excess of OH^- ions over the H^+ ions causes the solution to react alkaline.

When NH_4Cl is dissolved in water, the NH_4^+ ions tie up OH^- ions in the form of the weak base NH_4OH. Since HCl is a strong acid, the Cl^- ions do not tie up H^+ ions. As a result, the OH^- ion concentration of the solution is reduced, and by virtue of the resulting shift in the ionization equilibrium of H_2O, the concentration of H^+ ions is increased. This causes the solution to react acidic.

When NaCl is dissolved in water the Na^+ ions do not tie up OH^- ions because NaOH is a strong base, and the Cl^- ions do not tie up H^+ ions because HCl is a strong acid. As a result neither H^+ ions nor OH^- ions are removed from the solution, and it remains neutral.

When NH_4F is added to water the number of OH^- ions tied up by the weak base NH_4OH is approximately the same as the number of H^+ ions tied up by the weak acid HF. As a result the solution remains neutral.

The detailed reactions for each of the above examples are

$$\begin{aligned} &NaC_2H_3O_2 \rightarrow Na^+ + C_2H_3O_2^- \\ &H_2O \rightleftarrows OH^- + H^+ \\ &\qquad H^+ + C_2H_3O_2^- \rightleftarrows HC_2H_3O_2 \end{aligned}$$

$$\begin{aligned} &NH_4Cl \rightarrow NH_4^+ + Cl^- \\ &H_2O \rightleftarrows OH^- + H^+ \\ &\qquad OH^- + NH_4^+ \rightleftarrows NH_3 + H_2O \end{aligned}$$

$$\begin{aligned} &NH_4F \rightarrow NH_4^+ + F^- \\ &H_2O \rightleftarrows OH^- + H^+ \\ &\qquad H^+ + F^- \rightleftarrows HF \\ &\qquad OH^- + NH_4^+ \rightleftarrows NH_3 + H_2O \end{aligned}$$

$$\begin{aligned} &NaCl \rightarrow Na^+ + Cl^- \\ &H_2O \rightleftarrows OH^- + H^+ \end{aligned}$$

The net equations for the above reactions are

($NaC_2H_3O_2$)	$C_2H_3O_2^- + H_2O \rightleftarrows HC_2H_3O_2 + OH^-$
(NH_4Cl)	$NH_4^+ + H_2O \rightleftarrows NH_3 + H_2O + H^+$
(NH_4F)	$NH_4^+ + F^- + H_2O \rightleftarrows NH_3 + H_2O + HF$
($NaCl$)	no reaction

In the examples discussed above, the H^+ ions and OH^- ions are tied up in the form of a weak acid or a weak base. In the case of certain salts the H^+ ions or OH^- may be tied up in the form of stable complex ions. Thus when Na_2CO_3 is dissolved in water, the CO_3^{--} ions combine with the H^+ ions in the water equilibrium to form the stable hydrogen carbonate ion HCO_3^-. This reduces the concentration of H^+ ions and gives the solution an alkaline reaction. The net equation for the reaction is

$$CO_3^{--} + H_2O \rightleftarrows HCO_3^- + OH^-$$

When $AlCl_3$ is dissolved in water the Al^{+++} ions combine with OH^- ions to form a complex ion of the type $Al(OH)^{++}$. This reduces the concentration of OH^- ions and gives the solution an acidic reaction. The net equation for the reaction is

$$Al^{+++} + H_2O \rightleftarrows Al(OH)^{++} + H^+$$

Complex ions are discussed in Section 14.6.

If a salt yields as hydrolysis products a weak acid and a weak base, and if either or both are insoluble, the hydrolysis reaction is complete, with the result that the salt is decomposed when added to water. For example, Al_2S_3 yields $Al(OH)_3$, which is insoluble, and H_2S, which is slightly soluble. Consequently, a precipitate of Al_2S_3 will not form in the presence of water; it will be completely hydrolyzed to give H_2S gas and a precipitate of $Al(OH)_3$ according to the net equation

$$\mathbf{Al_2S_3} + 6\,H_2O = \mathbf{2\,Al(OH)_3} + 3\,H_2S\uparrow$$

Certain salts, notably $BiCl_3$ and $SbCl_3$, hydrolyze to give basic salts of the type BiOCl, and the degree of hydrolysis may be so great that the basic salt is precipitated.

$$Bi^{+++} + Cl^- + H_2O \rightleftarrows \mathbf{BiOCl} + 2\,H^+$$

The *hydrolysis constant* K_h can be calculated from the net equation,

(1) $$C_2H_3O_2^- + H_2O \rightleftarrows HC_2H_3O_2 + OH^-$$

(2) $$K_h = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-][H_2O]}$$

If both numerator and denominator of the right-hand term in (2) are multiplied by $[H^+]$ we obtain

(3) $$K_h = \frac{[HC_2H_3O_2]}{[C_2H_3O_2^-][H^+]} \times \frac{[H^+] \times [OH^-]}{[H_2O]}$$

But $\frac{[HC_2H_3O_2]}{[C_2H_3O_2^-][H^+]}$ is $1/K_i$ for acetic acid; its value, taken from Table 12.2, is $\frac{1}{1.8 \times 10^{-5}}$. Likewise, $\frac{[H^+] \times [OH^-]}{[H_2O]}$ is K_i for water; its value, taken from Table 12.2, is $\frac{1 \times 10^{-14}}{55.5}$. If these values are substituted in equation (3) we obtain

$$K_h \text{ (for the soluble acetate of any metal)} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 55.5}$$
$$= 1 \times 10^{-11}$$

The hydrolysis constants for the soluble, active-metal salts of all the weak acids listed in Table 12.2 can be calculated in the above manner.

It should be noted that the technique of resolving a given equilibrium constant into its component constants, which was used in calculating hydrolysis constants, can be employed in other calculations involving more than one equilibrium. To illustrate, suppose we are asked to calculate the acetate ion concentration of a 0.1 M solution of sodium formate ($NaCHO_2$) in 0.1 M $HC_2H_3O_2$. The net equation for the equilibrium that exists in such a solution is

$$CHO_2^- + HC_2H_3O_2 \rightleftarrows HCHO_2 + C_2H_3O_2^- \tag{4}$$

The equilibrium constant for this reaction is

$$K_{eq} = \frac{[HCHO_2] \times [C_2H_3O_2^-]}{[CHO_2^-] \times [HC_2H_3O_2]} \tag{5}$$

If we multiply both numerator and denominator by H^+ we obtain

$$K_{eq} = \frac{[HCHO_2]}{[H^+][CHO_2^-]} \times \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} \tag{6}$$

$$K_{eq} = \frac{1}{K_{HCHO_2}} \times K_{HC_2H_3O_2} \tag{7}$$

Substituting the values of the two constants from Table 12.2,

$$K_{eq} = \frac{1.8 \times 10^{-5}}{2 \times 10^{-4}} = 9 \times 10^{-2} \tag{8}$$

If we let X = the concentration in gram-ions per liter of $C_2H_3O_2^-$ ions in equation (4), the concentration in gram-ions per liter of CHO_2^-, $HC_2H_3O_2$, and $HCHO_2$ will be $0.1 - X$, $0.1 - X$, and X, respectively; these values and the calculated value of K_{eq} can be substituted in equation (5) to give

$$9 \times 10^{-2} = \frac{X^2}{(0.1 - X)^2}$$

Solving, $X = 2.3 \times 10^{-2}$ gram-ions per liter.

14.4 Indicators. Certain substances in solution have the unique property of changing color when the hydrogen ion concentration of the solution reaches a certain value. Because the hydrogen-ion-concentra-

tion range over which a specific substance always changes color is narrow and exact, this color change *indicates* that the hydrogen ion concentration of the solution lies in the narrow range. The substance can accordingly be used as an *indicator*. Some indicators change color on the acid side of neutrality, some on the basic side, a few at almost exact neutrality; the particular hydrogen ion concentration range in which the change occurs may differ greatly with different indicators, and no two indicators change color in exactly the same range. Familiar examples of indicators are litmus, phenolphthalein, and methyl orange. A large number of additional ones are available, some of which are listed in Table 14.2.

TABLE 14.2

*p*H RANGE OF TYPICAL INDICATORS

Indicator	*p*H *range in which color changes*	*Color changes observed within this p*H *range*
Methyl violet	0.1– 1.5	yellow to blue
Methyl violet	1.5– 3.2	blue to violet
Methyl orange	3.1– 4.4	red to orange yellow
Methyl red	4.2– 6.3	red to yellow
Bromthymol blue	6.0– 7.6	yellow to blue
Phenol red	6.8–8.4	yellow to red
Phenolphthalein	8.2–10.0	colorless to red
Thymolphthalein	9.3–10.4	colorless to blue
Alizarin yellow	10.1–12.1	yellow to lilac

Most indicators are weak organic acids or salts of such acids. The acid molecule (HIn) has one color and the anion which it yields (In^-) another color. The acid ionizes according to equation (1), while the salt hydrolyzes according to equation (2).

(1) $$\underset{\text{Color A}}{HIn} \rightleftarrows H^+ + \underset{\text{Color B}}{In^-}$$

(2) $$\underset{\text{Color B}}{In^-} + H_2O \rightleftarrows \underset{\text{Color A}}{HIn} + OH^-$$

If hydrogen ions (acid) are added to a solution of the indicator, the equilibrium is shifted to the left in equation (1) because of the common ion effect of the added H^+ ions, and to the right in equation (2) because of the combination of H^+ ions with OH^- ions to form H_2O. This results in each instance in formation of more HIn and less In^-. The solution will therefore acquire the color A of the acid molecule. If hydroxyl ions (base) are added, the equilibrium is shifted to the right in equation (1), because of the combination of OH^- ions with H^+ ions to form H_2O, and to the left in equation (2), because of the common ion effect of the added

OH^- ions. This results in each instance in formation of more In^- and less HIn. The solution will therefore acquire the color B of the In^- ions.

Because the indicator acids vary in strength, and therefore in per cent ionization, the concentration of H^+ and In^- ions in equation (1) and of HIn molecules and OH^- ions in equation (2) will vary from one indicator to another. The greater the concentration of In^- ions, the greater the concentration of added H^+ ions required to reduce the concentration of these In^- ions to the point where the color due to HIn molecules (color A) will predominate. The available indicators can thus be arranged in the order of the hydrogen ion concentration required to change them from the color B of the ion to the color A of the free acid. Such an arrangement is given in Table 14.2. The acidity or alkalinity range within which the color change takes place is expressed in *p*H units rather than in units of H^+ ion or OH^- ion concentration.

To illustrate how indicators can be used to determine the approximate *p*H of a colorless "unknown" solution, suppose bromthymol blue is added to the solution. If a yellow color is produced, the *p*H is *6.0 or lower:* if a blue color results, the *p*H is *7.6 or higher.* Suppose a blue color results; if we now add phenolphthalein to a separate sample of the solution and find that it remains colorless we know that the *p*H is *less than 8.2.* In other words, the *p*H is somewhere between 7.6 and 8.2. By the use of additional indicators not given in the table it may be possible to narrow the *p*H down to a very small range.

In addition to their universal use in titration, indicators are widely used in industry for determining the approximate acidity or alkalinity of various solutions. There are available "indicator papers" which have been impregnated with several indicators which, taken together, cover a very broad *p*H range; by simply dipping the paper into the solution to be tested, noting the color produced, and consulting a table similar to Table 14.2, which is furnished by the manufacturers of the paper, the approximate *p*H of any solution can be determined in one simple operation.

It should be noted that some indicators are weak bases (InOH) which ionize according to equation (3).

(3) $$\underset{\text{Color B}}{InOH} \rightleftarrows \underset{\text{Color A}}{In^+} + OH^-$$

A few indicators exist in so-called A and B isomeric modifications whose colors differ.

(4) $$\underset{\text{Color A}}{\text{A form}} \rightleftarrows \underset{\text{Color B}}{\text{B form}}$$

The equilibrium point and hence the color are functions of the H^+ ion concentration of the solution.

14.5 Buffer action. Hydrochloric acid is a strong acid; that means that it is 100% ionized. A liter of 0.01 molar hydrochloric acid will therefore contain 0.01 gram-ion of H^+ ions. If a quantity of solid Na_3PO_4 is dissolved in 0.01 *M* HCl, the concentration of the hydrogen ions in the acid will be reduced; this can be proved by demonstrating that the rate at which a quantity of magnesium metal liberates hydrogen from the acid to which Na_3PO_4 has been added is slower than the rate at which the same quantity of magnesium liberates hydrogen from pure 0.01 *M* HCl. The rate at which a given quantity of magnesium liberates hydrogen from an acid is proportional to the hydrogen ion concentration of the acid; therefore a slower rate of evolution of H_2 means a lower concentration of hydrogen ions.

The reduction in the concentration of the hydrogen ions when Na_3PO_4 is added can be accounted for in the following manner: Na_3PO_4 is a salt and therefore is a strong electrolyte. That means that when it is dissolved in water it yields a great many PO_4^{---} ions. These PO_4^{---} ions will combine with the H^+ ions from the 0.01 *M* HCl to form the weak acid H_3PO_4. Since H_3PO_4 is a weak acid it is not ionized to any great extent. That means that many of the H^+ ions from the HCl have been tied up in the form of H_3PO_4 molecules. As a result, the hydrogen ion concentration of the solution has been reduced. The detailed equation for the reaction is

$$\begin{aligned} HCl &\rightarrow H^+ + Cl^- \\ Na_3PO_4 &\rightarrow PO_4^{---} + 3\,Na^+ \\ PO_4^{---} &+ 3\,H^+ \rightleftarrows H_3PO_4 \end{aligned}$$

Although the Na_3PO_4 has reduced the concentration of hydrogen ions in the 0.01 *M* HCl, it has not changed the total available hydrogen in the solution. This can be proved by demonstrating that the total volume of hydrogen gas that an excess of magnesium will liberate from a liter of 0.01 *M* HCl to which Na_3PO_4 has been added is exactly the same as the volume of hydrogen that an excess of magnesium will liberate from a liter of pure 0.01 *M* HCl. The fact that the total available hydrogen has not been changed by addition of Na_3PO_4 can be accounted for in the following way: H_3PO_4 ionizes according to the equation

$$H_3PO_4 \rightleftarrows 3\,H^+ + PO_4^{---}$$

When hydrogen ions are removed from solution by the magnesium metal

in accordance with the reaction

$$Mg + 2\,H^+ = Mg^{++} + H_2$$

the ionization equilibrium for H_3PO_4 will be shifted to the right. Eventually all the H_3PO_4 will have disappeared and the hydrogen ions will all have been given off as hydrogen gas. The PO_4^{---} ions take hydrogen ions out of solution and store them as H_3PO_4 molecules, but these hydrogen ions are available when they are needed.

The soluble salt of any weak acid will reduce the concentration of hydrogen ions in the same way that Na_3PO_4 does.

Just as a soluble salt of a weak acid will tie up H^+ ions, the soluble salt of a weak base will tie up OH^- ions. Ammonium chloride will, for example, reduce the OH^- ion concentration of a solution of NaOH or KOH. The NH_4^+ ions from the NH_4Cl will combine with the OH^- ions from the NaOH and tie them up in the form of the weak base NH_4OH. The concentration of OH^- ions in the solution will thereby be reduced, but the total available alkalinity will not be altered.

The ability of the salt of a weak acid to tie up hydrogen ions in the form of molecules of the weak acid, and the ability of the salt of a weak base to tie up hydroxyl ions as molecules of the weak base, is the basis of a phenomenon known as *buffer action*. If a small amount of strong acid is added to pure water, or to a dilute solution of acid in water, the hydrogen ion concentration of the water or solution is noticeably increased. If the same small amount of acid is added to the same amount of solution containing a weak acid and the soluble salt of that acid, the increase in hydrogen ion concentration is so slight that, for all practical purposes, it is negligible. The anions of the salt of the weak acid have taken the H^+ ions as fast as they were added and have tied them up in the form of molecules of the weak acid. The net result is that the hydrogen ion concentration has changed only very slightly. If now a small amount of a strong base is added to the solution, the hydrogen ion concentration will still remain practically unchanged; as fast as the OH^- ions react with and remove H^+ ions, more of the weak acid that is present in the solution ionizes. As a result the H^+ ions that are removed are immediately replaced and their concentration remains practically constant. This maintenance of a practically constant hydrogen ion concentration in spite of the addition of hydrogen ions or hydroxyl ions is called *buffer action*. The solution of the substance which is capable of exerting the buffer action is called a *buffer solution*. Just as a solution of a weak acid and the salt of that acid will serve as a buffer for an acid system, a solution of a weak base and a salt of that base will buffer an alkaline system. Some common buffer solutions are sodium acetate-

acetic acid, sodium phosphate-phosphoric acid, sodium citrate-citric acid, and ammonium chloride-ammonium hydroxide.

14.6 Complex ions. When a simple ion combines with one or more other ions or with one or more neutral molecules to form a new ion, this new ion is called a *complex ion.* The complex hydronium ion H_3O^+ is formed when an H^+ ion combines with a molecule of H_2O. A copper ion combines with 4 NH_3 molecules to form the complex ion $Cu(NH_3)_4^{++}$, while an Fe^{+++} ion combines with 6 SCN^- ions to form the $Fe(SCN)_6^{---}$ ion. Other complex ions that will be encountered are $Ag(NH_3)_2^+$, $PbCl_4^{--}$, $Cd(NH_3)_4^{++}$, $Cd(CN)_4^{--}$, $Cu(CN)_2^-$, SnS_3^{--}, SbS_3^{---}, AsS_4^{---}, $Ni(NH_3)_6^{++}$, $Co(NH_3)_6^{+++}$, $FeCl_4^-$, $Zn(NH_3)_4^{++}$, $Fe(CN)_6^{----}$, $Al(OH)_4^-$, $Zn(OH)_4^{--}$, $Cr(OH)_4^-$, $Sn(OH)_4^{--}$, $Sn(OH)_6^{--}$, $Co(SCN)_4^{--}$, FeF_6^{---}, $HgCl_4^{--}$, and $CuCl_4^{--}$.

All complex ions are unstable to a greater or lesser degree, and dissociate, equilibrium-wise, in characteristic fashion to give, usually, the ions or molecules from which they were formed. Table 14.3 gives the dissociation equations for a number of complex ions.

TABLE 14.3

COMPLEX ION EQUILIBRIA

Equation	*Instability constant*
$Ag(NH_3)_2^+ \rightleftarrows Ag^+ + 2\ NH_3$	6×10^{-8}
$Ag(CN)_2^- \rightleftarrows Ag^+ + 2\ CN^-$	1×10^{-21}
$Cu(NH_3)_4^{++} \rightleftarrows Cu^{++} + 4\ NH_3$	4.6×10^{-14}
$Cu(CN)_2^- \rightleftarrows Cu^+ + 2\ CN^-$	5×10^{-28}
$Cd(NH_3)_4^{++} \rightleftarrows Cd^{++} + 4\ NH_3$	2.5×10^{-7}
$Cd(CN)_4^{--} \rightleftarrows Cd^{++} + 4\ CN^-$	1.4×10^{-19}
$Co(NH_3)_6^{+++} \rightleftarrows Co^{+++} + 6\ NH_3$	1.2×10^{-5}
$Fe(SCN)_6^{---} \rightleftarrows Fe^{+++} + 6\ SCN^-$	3.1×10^{-4}
$Fe(CN)_6^{----} \rightleftarrows Fe^{++} + 6\ CN^-$	1×10^{-37}
$Ni(NH_3)_6^{++} \rightleftarrows Ni^{++} + 6\ NH_3$	4.8×10^{-8}
$Zn(NH_3)_4^{++} \rightleftarrows Zn^{++} + 4\ NH_3$	2.6×10^{-10}

Since the above equations represent true equilibrium reactions, their equilibrium constants can be represented in the conventional manner. The mass law equation when applied to these reactions yields, for the equation

$$Ag(NH_3)_2^+ \rightleftarrows Ag^+ + 2\ NH_3$$

for example, the expression

$$K_{Inst.} = \frac{[Ag^+] \times [NH_3]^2}{[Ag(NH_3)_2^+]}$$

For a complex ion which is very stable, and hence is only slightly dissociated, the quantities in the numerator will be very small, the quantity in the denominator will be relatively large, and the value of K will be very small. On the other hand, a complex ion that is relatively unstable and hence dissociates to a fairly high degree will have a relatively large K. The value of K is therefore a measure of the instability of the ion; if K is very small, the ion is very stable, if K is large, the ion is relatively instable. For that reason K is called the *instability constant* and is designated by the symbol $K_{Inst.}$ The instability constants for the equations cited are given in Table 14.3. Certain of these ions, it will be noted, are extremely stable, while others are quite unstable.

Having considered a number of specific complex ions, certain questions arise. How can an ion such as Co^{+++}, for example, hang on to 6 molecules of NH_3? Why does the copper complex ion with ammonia contain 4 molecules of NH_3, while the nickel complex contains 6 molecules?

Complex ions are presumed to form in accordance with a theory which postulates that over and above its usual electrovalence each ion has a so-called auxiliary valence which gives it a definite *capacity* for combining with, or attaching to itself, other ions or molecules. This auxiliary valence results in the attached ions or molecules being bound more or less firmly to the central ion by a coordinate bonding. The maximum number of ions or molecules that an ion is able to attach to itself is called its *coordination number*. Thus Co^{+++} and Ni^{++} each have a coordination number of 6; this is deduced from the fact that they combine with 6 molecules of NH_3. The ion Cu^{++} can combine with a maximum of 4 molecules of NH_3, and is presumed therefore to have a coordination number of 4. The belief that Co^{+++} has a coordination number of 6 is strengthened by the fact that it forms the following complex ions: $Co(SCN)_6^{---}$, $Co(NO_2)_6^{---}$, $Co(NH_3)_5Cl^{++}$, $Co(NH_3)_4Cl_2^+$, $CoCl_4(H_2O)_2^-$. As the last four of these cobalt complexes indicate, the attached ions or molecules need not all be of the same species.

The B group metals show strong tendency to form complex ions. In contrast the A group metals form very few complexes. Since the outstanding structural difference between the B group and A group elements lies in the fact that the latter are built up by addition of electrons directly to the valence shell, while the former are generally built up by addition of electrons to the subshells below the valence shell, the tendency to form complex ions appears to be associated, somehow, with the presence of unfilled subshells below the valence shell. It should be

noted also that the ions that form complexes have small diameters, while those that do not form complexes have larger diameters.

The charge carried by the complex ion is the algebraic sum of the charges on the central ion and the attached ions or molecules. Thus $Co(SCN)_6^{---}$ has a charge of -3 because the 1 Co^{+++} and 6 SCN^- give a net value of -3. One Co^{+++} plus 1 Cl^- plus 5 neutral NH_3 give the $Co(NH_3)_5Cl^{++}$ complex a net charge of $+2$.

In water solution, and in the absence of a more readily attachable group or ion, nearly all central ions that tend to form complexes will coordinate with water molecules. That means that any and every complexable ion that is not coordinated, either fully or in part, with other ions or groups, is coordinated, in whole or in part, with H_2O. Speaking exactly, aluminum ions are $Al(H_2O)_6^{+++}$, not simply Al^{+++}, and the $CrCl^{++}$ ion is really the $Cr(H_2O)_5Cl^{++}$ ion. Because it would become tedious and cumbersome to indicate always the degree of hydration of an ion, and because the degree of hydration has no effect on the stoichiometric behavior of an ion as it is represented in a balanced equation, we shall not, except in rare instances, represent a simple or partially coordinated ion in its hydrated form. We shall, however, have the same understanding that has already been declared for the H^+ ion. We acknowledge that it is hydrated but we will not represent it as such.

The exact composition of the complex ions that are formed when the two reactants are brought together in solution may vary with the concentration of the complexing species. Thus when solid AgI is treated with a solution of KI of moderate concentration, the predominant complex species is AgI_2^-. As the concentration of I^- ions is increased, the AgI_3^{--} ions become the predominant species, although AgI_2^- ions are still present. The equilibrium picture is probably represented by the equations

$$Ag^+ + 2\ I^- \rightleftarrows AgI_2^-$$
$$AgI_2^- + I^- \rightleftarrows AgI_3^{--}$$

It will be the policy in this book to use that complex ion formula that experimental evidence indicates is the one that predominates at high concentrations of the complexing ion.

The constituent parts of a complex ion are named in the following order: acid radical, neutral molecule, central cation. In a negative ion the name of the central atom ends in *ate*, in a positive ion it retains its common name. A Roman numeral shows the oxidation state of the central atom. Thus $Co(NH_3)_6^{+++}$ is the hexamminecobalt(III) ion, $Co(NH_3)_5Cl^{++}$ is the chloropentamminecobalt(III) ion, $Fe(CN)_6^{---}$ is the hexacyanoferrate(III) ion, $FeCl_4^-$ is the tetrachloroferrate(III) ion,

$FeCl^{++}$ is the monochloroiron(III) ion, $Sn(OH)_4^{--}$ is the tetrahydroxostannate(II) ion, $Sn(OH)_6^{--}$ is the hexahydroxostannate(IV) ion, and $NaAg(CN)_2$ is sodium dicyanoargentate. Note that the *ite* ending, which is used to designate a lower oxidation state of the central element in a simple ion such as sulf*ite*, SO_3^{--} (and sulf*ate*, SO_4^{--}), is not used in naming complex ions; only the *ate* ending is used, the oxidation state being indicated by a Roman numeral.

14.7 Amphoteric hydroxides. Among the complex ions that will be encountered, $Zn(OH)_4^{--}$, $Sn(OH)_4^{--}$, $Cr(OH)_4^{-}$, and $Al(OH)_4^{-}$ are of particular interest because their formation illustrates the *amphoteric character* of the hydroxides of the metals involved. Using zinc as an example, if a solution of sodium hydroxide is added dropwise to a solution of a soluble zinc salt, a white precipitate, $Zn(OH)_2$, will first form. If the dropwise addition of the sodium hydroxide solution is continued, the solid $Zn(OH)_2$ will gradually dissolve until finally a water-clear solution is obtained. This clear solution is found to contain the complex ion $Zn(OH)_4^{--}$. As a general rule if a solid compound redissolves in an excess of a reagent that was responsible for its formation in the first place, complex ions have been formed. The net equation to account for their formation when excess base is added to the precipitate of $Zn(OH)_2$ is

$$\mathbf{Zn(OH)_2} + 2\ OH^- \rightleftarrows Zn(OH)_4^{--} \text{ (tetrahydroxozincate ion)}$$

The $Zn(OH)_2$ that is precipitated when a solution of a zinc salt is treated with NaOH will dissolve in any strong acid in accordance with the following net equation.

$$Zn(OH)_2 + 2\ H^+ = Zn^{++} + 2\ H_2O$$

There is nothing unusual about this latter reaction; $Zn(OH)_2$ is the hydroxide of a metal, and metal hydroxides react with acids to form salts and water. The solubility of $Zn(OH)_2$ in excess sodium hydroxide is, however, distinctive. It means that $Zn(OH)_2$ will react with either a strong acid or a strong base. A hydroxide that has the property of reacting with either a strong acid or a strong base is said to be *amphoteric*.

The hydroxides of aluminum, chromium, tin, lead, and antimony, like $Zn(OH)_2$, are amphoteric. They react with strong acids in the manner typical of the basic hydroxides of metals. They react with strong bases as does $Zn(OH)_2$ to form complex ions whose formulas will, for the sake of simplicity, all be represented as being made up of 4 OH groups, namely $Al(OH)_4^{-}$, $Cr(OH)_4^{-}$, $Sn(OH)_4^{--}$, $Pb(OH)_4^{--}$, and $Sb(OH)_4^{-}$. These formulas all correspond to the general formula

$M(OH)_4^{-x}$. They are not intended to be exact; rather, they are intended to show that the hydroxide of the metal is amphoteric.

The hydroxo complexes exist in equilibrium with their ions in typical complex ion fashion as represented by the equation

$$Pb(OH)_4^{--} \rightleftarrows Pb^{++} + 4\ OH^-$$

If a solution of a strong acid is added dropwise to a solution containing any one of the above-mentioned complex hydroxo ions, the hydroxide of the metal is completely precipitated. On further addition of acid the hydroxide dissolves to form a solution containing the cation of the metal. This behavior indicates that there exists an equilibrium of the type represented by the net equation

$$\mathbf{Cr(OH)_3} + OH^- \text{ (excess)} \rightleftarrows Cr(OH)_4^-$$

The hydrogen ions (acid) that are added remove OH^- ions, and thereby reduce the rate of reaction to the right. This causes the equilibrium point to be shifted to the left, which means that $Cr(OH)_3$ precipitates out. When the excess OH^- ions have all been neutralized, the acid dissolves the hydroxide in the conventional manner indicated by the net equation

$$\mathbf{Cr(OH)_3} + 3\ H^+ = Cr^{+++} + 3\ H_2O$$

If solutions of the complex hydroxo ions formed by dissolving the amphoteric hydroxides in sodium hydroxide are concentrated by evaporation, solid salts of compositions represented by the formulas Na_2ZnO_2, Na_2SnO_2, and $NaAlO_2$ will crystallize out. This indicates that the solutions may have contained the ions ZnO_2^{--}, SnO_2^{--}, and AlO_2^-. The presence of these ions can be accounted for by equilibria of the type

$$Sn(OH)_4^{--} \rightleftarrows SnO_2^{--} + 2\ H_2O$$

The question will arise as to why, among the many metal hydroxides, the six discussed above should be amphoteric while the others are not. We will find, if we examine the periodic table, that all but one of the six metals in question lie along the borderline between the characteristically nonmetallic elements in the upper right section of the table and the more characteristically metallic elements that occupy the rest of the table. Accordingly, their hydroxides, although predominantly basic, are also somewhat acidic in character. These borderline elements are sometimes referred to as *metalloids*.

Questions and Problems

1. Define or describe, and illustrate each of the following: ion product; K_{H_2O}; pH; hydrolysis; hydrolysis constant; indicator; buffer;

buffer solution; $NaC_2H_3O_2$—$HC_2H_3O_2$ buffer; complex ion; amphoteric hydroxide.

2. Arrange the following solutions in the order of decreasing hydrogen ion concentration: (a) distilled water; (b) 0.1 *M* KOH; (c) 0.1 *M* HCl; (d) 0.1 *M* $HC_2H_3O_2$; (e) 0.1 *M* NH_4OH; (f) 0.1 *M* KOH containing 1 g/l of NH_4Cl; (g) 0.1 *M* NH_4OH containing 10 g/l of NH_4Cl; (h) 0.1 *M* $HC_2H_3O_2$ containing 1 g/l of $NaC_2H_3O_2$; (i) 0.1 *M* HCl containing 1 g/l of Na_3PO_4.

3. Arrange the following solutions in the order of increasing *p*H: (a) 0.1 *M* NaCl; (b) 0.1 *M* HCl; (c) 0.1 *M* KOH; (d) 0.05 *M* Na_2CO_3; (e) 0.1 *M* NH_4Cl.

4. What is the *p*H of each of the following solutions? (a) 0.001 *M* HCl, 100% ionized; (b) 0.005 *M* H_2SO_4, 100% ionized; (c) 0.01 *M* HBr, 100% ionized; (d) 0.001 *M* KOH, 100% ionized; (e) 1×10^{-7} *M* HCl, 100% ionized; (f) 1×10^{-8} *M* HCl, 100% ionized; (g) 0.0005 *M* $Ba(OH)_2$, 100% ionized; (h) 0.005 *M* $HC_2H_3O_2$, 2% ionized; (i) 0.1 *M* KCl, 100% ionized.

5. Arrange the following solutions in the order of increasing *p*H: (a) 0.01 *M* NaOH; (b) 0.01 *M* NH_4OH; (c) 0.01 *M* NH_4Cl; (d) 0.01 *M* $KHSO_4$; (e) 0.01 *M* K_2SO_4; (f) 0.01 *M* H_2SO_4.

6. A solution gave a yellow color with both methyl red and bromthymol blue indicators. What was its approximate *p*H?

7. Which solution in each of the following pairs has the higher *p*H? (a) 0.1 *M* HF, 0.1 *M* HI; (b) 0.1 *M* $CuCl_2$, 0.1 *M* $CaCl_2$; (c) 0.1 *M* NaOH, 0.1 *M* NH_4OH; (d) 0.1 *N* $HC_2H_3O_2$, 0.1 *N* $HC_2H_3O_2$ in 1 *M* $NaC_2H_3O_2$; (e) 0.1 *M* HCl, 0.1 *M* H_2SO_4; (f) 0.1 *N* K_2SO_4, 0.1 *N* K_2SO_3; (g) Distilled water, 1.0 *N* NaCl; (h) 0.1 *M* Na_2SO_4, 0.1 *M* $NaHSO_4$; (i) 0.1 *N* HCl, 0.1 *N* HCl in 1.0 *M* $NaC_2H_3O_2$; (j) 0.1 *M* NH_4OH, 0.1 *M* NH_4OH in 1.0 *M* NH_4Cl; (k) 0.1 *M* KOH, 0.1 *M* KOH in 1.0 *M* NH_4Cl; (l) 10^{-8} *M* HCl, 10^{-6} *M* KOH, both 100% ionized; (m) 10^{-7} *M* HCl, 10^{-7} *M* KOH, both 100% ionized.

8. Would the following substances, dissolved in distilled water, give acidic, basic, or neutral solutions? (a) NH_4Cl; (b) SO_2; (c) H_2; (d) KBr; (e) Na_2S; (f) $NaHSO_4$; (g) $FeCl_3$; (h) MgO; (i) NH_4F; (j) Al_2S_3; (k) K_2CO_3; (l) $Pb(NO_3)_2$; (m) $NaC_2H_3O_2$; (n) $CuSO_4$; (o) CO_2.

9. Account for each of the following experimental facts. Give detailed ionic equations and net equations for all reactions involved. (a) One hundred milliliters of 0.1 *M* HCl which is 1 *M* in Na_3PO_4 liberates hydrogen gas more slowly when treated with excess Mg than does

100 ml of pure 0.1 *M* HCl. The same volume of H_2 is liberated from both solutions. (b) One hundred milliliters of 1 *M* $HC_2H_3O_2$ which is 1 *M* in $NaC_2H_3O_2$ liberates CO_2 gas more slowly when treated with excess finely divided $CaCO_3$ than does 100 ml of pure 1 *M* $HC_2H_3O_2$. The same volume of CO_2 gas is liberated from both solutions. (c) When NH_4OH is added to 100 ml of 0.1 *M* $MgCl_2$, a precipitate of $Mg(OH)_2$ forms, but when the same quantity of NH_4OH is added to 100 ml of 0.1 *M* $MgCl_2$ in 1 *M* NH_4Cl, no precipitate forms. (d) The hydroxide $Mg(OH)_2$, which is not soluble in water, is soluble in 1 *M* NH_4Cl. (e) Solutions of the normal salts NaF, NH_4Cl, $NH_4C_2H_3O_2$, and NaCl react alkaline, acidic, neutral, and neutral, respectively, to litmus paper. (f) The *p*H of a solution of acetic acid and sodium acetate is not appreciably changed when small amounts of either HCl or NaOH are added. (g) When 2 *M* NaOH is added dropwise to 0.1 *M* $ZnCl_2$, a white precipitate first forms, but on further addition of NaOH the precipitate dissolves to form a clear solution. When 2 *M* HCl is added dropwise to this clear solution, a white precipitate first forms, but on further addition of HCl this precipitate dissolves to form a clear solution. (h) When 2 *M* NH_4OH is added dropwise to 0.1 *M* $CuSO_4$, a pale blue precipitate first forms, but on further addition of NH_4OH the precipitate dissolves to form a deep blue solution. When 2 *M* H_2SO_4 is added dropwise to this deep blue solution a pale blue precipitate first forms, but on further addition of H_2SO_4 this precipitate dissolves to form a light blue solution. (i) A saturated solution of $AgC_2H_3O_2$ was prepared by shaking solid $AgC_2H_3O_2$ with distilled water. A drop of 0.2 *M* $AgNO_3$ was added to one 10-drop sample of this saturated solution, while a drop of 0.2 *M* $NaC_2H_3O_2$ was added to another. A white precipitate formed in each sample.

10. When a water solution of ammonia is added to solid silver chloride, the following equilibrium is established:

$$AgCl + 2\,NH_4OH \rightleftarrows Ag(NH_3)_2^+ + Cl^- + 2\,H_2O$$

How would the amount of solid AgCl present in this equilibrium be affected (increased, decreased, remain the same) by adding: (a) HNO_3 (b) HCl (c) NH_3 (d) NaCl (e) heat?

11. Calculate the *p*H of each of the following solutions:
    (a) One containing 4×10^{-3} gram-ions of H^+ per liter.
    (b) One containing 6×10^{-4} g of H^+ per liter.
    (c) One containing 2.5×10^{-3} gram-ion of OH^- per liter.
    (d) 0.1 *M* HCl which is 100% ionized.
    (e) 0.01 *M* $HCHO_2$ which is 13.4% ionized.
    (f) 0.1 *M* NH_4OH which is 4.1% ionized.
    (g) 0.001 *M* $Ba(OH)_2$ which is 100% ionized.

12. A solution of 0.001 *M* HF has a *p*H of 4. Calculate the per cent ionization of the HF.

13. A 0.01 *M* solution of the acid H_2X has a *p*H of 3. Calculate the ionization constant of the reaction $H_2X \rightleftarrows 2\ H^+ + X^{--}$.

14. Calculate the hydrogen ion concentration of a solution whose *p*H is 3.2.

15. The ionization constant for formic acid, $HCHO_2$, is 2×10^{-4}. Calculate the hydrolysis constant for sodium formate.

16. Calculate the concentration of fluoride ions in a 0.2 *M* solution of $NaNO_2$ in 0.1 *M* HF.

17. The weak base NH_4OH has an ionization constant of 1.8×10^{-5}. What is the hydroxyl ion concentration of a liter of solution containing 0.25 mole of NH_4OH and 0.75 mole of NH_4Cl? The NH_4Cl is 100% ionized.

CHAPTER 15

Electrolysis

The ability of melted electrovalent compounds and solutions of electrolytes to conduct electricity, and the fact that in the conductivity process the positive ions (cations) are transported to the negative electrode (cathode) of the circuit, while the negative ions (anions) are transported to the positive electrode (anode), is put to practical use in a wide variety of industrial electrolysis processes. A few typical processes are discussed in this chapter.

15.1 Preparation of metals and nonmetals by electrolysis of melted salts. The active metals in group IA and IIA are prepared commercially by electrolysis of their melted chlorides. Using the electrolysis of NaCl as an example, the positive Na^+ ions migrate to the negative pole, while the negative Cl^- ions are transported to the positive

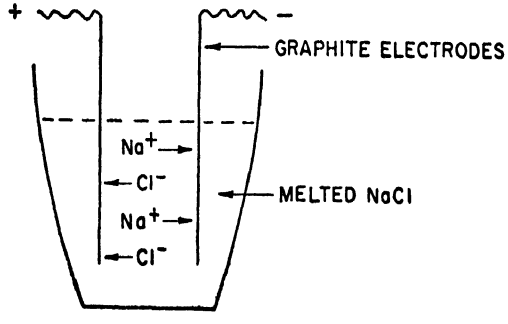


Figure 15.1. Electrolysis of melted sodium chloride.

pole (see Figure 15.1). When the Na^+ ions reach the negative pole, each picks up an electron and becomes an atom of metallic sodium. This sodium, in the molten condition and protected from being oxidized by the air, is drawn off and cast into molds (see Figure 15.2). The Cl^- ions give up their electrons to the positive graphite electrode and form Cl_2 gas. The graphite electrode is not acted upon to any great extent by the chlorine. The detailed reactions involved are

$$2\ Na^+ + 2\ \text{electrons} = 2\ Na$$
$$2\ Cl^- = Cl_2 + 2\ \text{electrons}$$

Bromine, iodine, and fluorine are obtained in similar fashion when their fused binary salts are electrolyzed.

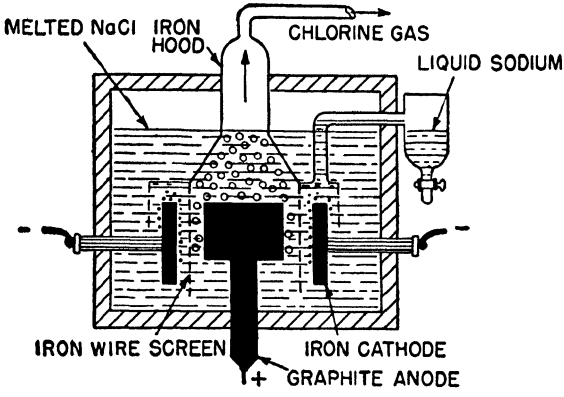


Figure 15.2. Downs cell for manufacture of sodium and chlorine by electrolysis of melted sodium chloride. The chlorine and sodium do not come in contact with each other or with the air. The melted sodium is insoluble in NaCl and is less dense than the molten salt. As a result it rises to the top of the bath and can be drawn off and cast into sticks.

15.2 Preparation of NaOH, H_2, and Cl_2 by electrolysis of an aqueous solution of NaCl. Graphite (carbon) electrodes are used. The Cl^- ions migrate to the positive pole, give up their extra electron and escape, and are collected as Cl_2 gas. The H^+ ions from the water migrate to the negative pole where each picks up an electron and escapes as hydrogen gas. Although Na^+ ions are present in the solution sodium metal is not deposited. This is in accordance with the general rule that a chemical process follows the path of least resistance. Since hydrogen is less electropositive than sodium, the reduction of H^+ ions to elemental hydrogen goes on more easily than does the reduction of Na^+ ions to free sodium.

The net equation for the reaction process is

$$2\ Cl^- + 2\ H_2O + 2\ Na^+ = Cl_2\uparrow + H_2\uparrow + 2\ OH^- + 2\ Na^+$$

Evaporation of the product solution to dryness yields solid NaOH. About $2\frac{1}{2}$ million tons of NaOH are prepared annually in the United States by this process.

15.3 Preparation of O_2 and H_2 by electrolysis of a solution of H_2SO_4 in water. Platinum anodes and graphite cathodes are used. The H^+ ions derived from the ionization of H_2SO_4 are transported to the negative pole, where each picks up an electron and forms H_2 gas. Oxygen gas is liberated at the positive pole; just what happens to account for this liberation is not known for certain.

The over-all reaction may be represented by the equation

$$2\,H^+ + SO_4^{--} + 2\,H_2O = 2\,H_2 + O_2 + 2\,H^+ + SO_4^{--}$$

15.4 Electroplating of metals. The article to be electroplated (with copper for example) is made the negative electrode. The electrolyte is generally copper sulfate and the positive pole is a slab of copper (see Figure 15.3). The copper ions migrate to the negative

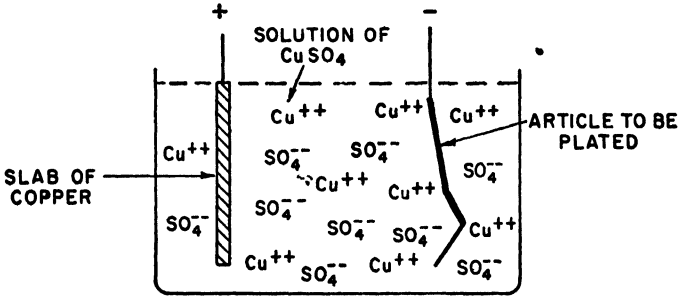


Figure 15.3. Copper plating bath.

electrode (the article to be plated), pick up 2 electrons, and are deposited as metallic copper. At the positive pole copper metal goes into solution to form Cu^{++} ions; the exact role of the SO_4^{--} ion in this solution process is not well understood.

The net equations for the reactions at each electrode are

At the negative pole: $Cu^{++} + 2$ electrons $=$ **Cu**

At the positive pole: **Cu** $= Cu^{++} + 2$ electrons

All metal plating follows the pattern outlined above, although the type of electrolyte solution may vary from one metal to another. When a solution of the cyanide of the metal is used, as is the case in gold and silver plating, the cation is tied up, largely in the form of a fairly stable complex ion such as $Ag(CN)_2^-$. This keeps the concentration of Ag^+ ions in the solution low. A low concentration of Ag^+ ions is desirable for the formation of a good deposit of silver. The detailed equations involved are

$$Ag(CN)_2^- \rightleftarrows Ag^+ + 2\ CN^-$$

$$Ag^+ + \text{electron} = \mathbf{Ag}$$

In *electrotyping*, the object to be plated is a wax impression of the page of type which is to be reproduced. The surface of the impression is covered with a film of graphite dust to make it a conductor. A thin sheet of copper is then electrodeposited over the graphite-coated wax impression. This sheet is "backed" with type metal to give a rigid "plate" which is then used for printing.

15.5 Electrorefining of metals. Impure metals, copper for example, are refined (purified) by making them the positive electrodes (anodes) in an electrolytic cell in which "starting sheets" of pure metal are the negative electrodes (cathodes). The electrolyte is a salt of the metal. The reactions that take place are identical with those that occur in electroplating. The impure metal goes into solution to form the metal ion.

$$\mathbf{Cu} = Cu^{++} + 2 \text{ electrons}$$

At the same time, metal ions are removed from solution and deposited on the negative electrode as pure metal.

$$Cu^{++} + 2 \text{ electrons} = \mathbf{Cu}$$

The less reactive impurities, gold and silver, do not dissolve, but drop off the anode as the copper goes into solution and are precipitated in the bottom of the cell as electrolytic "mud." Metals more electropositive than copper go into solution and remain there as ions; since they are more electropositive than copper, these metals require for their electrodeposition from solution a current of higher voltage than that required to deposit copper. If the correct voltage is maintained, copper alone will be deposited.

15.6 Preparation of specific substances by electrolytic oxidation or reduction. This type of preparation depends on the fact that oxidation, resulting from loss of electrons or liberation of oxygen or chlorine, always takes place at the anode, while reduction, resulting from gain of electrons or liberation of hydrogen, occurs at the cathode. Thus when a solution of H_2SO_4 is electrolyzed by using PbO electrodes, oxidation to PbO_2 occurs at the positive pole, while reduction to Pb takes place at the cathode. The net reactions at each pole are

At anode:

$$\mathbf{PbO} (+ SO_4^{--}) + H_2O = \mathbf{PbO_2} + 2\ H^+ (+ SO_4^{--}) + 2 \text{ electrons}$$

At cathode:

$$\mathbf{PbO} + 2\,H^+ + 2 \text{ electrons} = \mathbf{Pb} + H_2O$$

15.7 Faraday's law. Elements are electrodeposited or electrodissolved in accordance with *Faraday's law*, which states that *1 faraday of electricity, when passed through a solution of an electrolyte, will deposit, or liberate, 1 gram-equivalent weight of an element.* One faraday of electricity is 96,500 coulombs. One coulomb is 1 ampere of current flowing for 1 second.

Faraday's law means that the concept of equivalence discussed in Section 13.14 applies to the electrochemical behaviour of elements as well as to their chemical behavior. Not only will 1 gram-equivalent weight of one element combine with or replace 1 gram-equivalent weight of any other element, but the quantity of electricity (1 faraday) that will deposit or dissolve 1 gram-equivalent weight of one element will deposit or dissolve 1 gram-equivalent weight of every other element. Thus 1 faraday will deposit 107.9 g (1 gram-atom) of silver from a solution of $AgNO_3$, 31.8 g ($\frac{1}{2}$ gram-atom) of copper from a solution of $CuSO_4$, and 17.3 g ($\frac{1}{3}$ gram atom) of chromium from a solution $CrCl_3$.

It follows from what has been stated above that the weights of two elements that are deposited by the same amount of electricity will be proportional to their equivalent weights. Thus, since the equivalent weights of copper(II) and silver are, respectively, 31.8 and 107.9, the weight of the copper deposited by a certain amount of electricity will be to the weight of the silver deposited by the same amount of electricity as 31.8 is to 107.9. The quantity of copper deposited by a given amount of electricity from a solution of Cu^+ ions will be twice as great as the quantity deposited from a solution of Cu^{++} ions.

Faraday's law assumes that the electrolysis process is 100% efficient. In the majority of electrodepositions the current efficiency is very close to 100%.

Questions and Problems

1. Define or describe, and illustrate: anode; cathode; electrolysis; electroplating; electrodeposition; electrorefining.

2. Discuss what is believed to take place in each of the following processes, giving detailed and net equations.

(a) Electrolysis of melted KBr.
(b) Electrolysis of an aqueous solution of KCl.
(c) Electrolysis of a water solution of H_2SO_4.
(d) Electrorefining of copper using $CuSO_4$ as the electrolyte.
(e) Electrodeposition of silver from a solution of $Ag(CN)_2^-$.

3. How many coulombs of electricity will be required to deposit 20.0 g of copper from a solution of $CuSO_4$?

4. A current of 3.00 amp was allowed to flow through a solution of $AgNO_3$ for 8 hr. How many grams of silver were deposited?

5. A certain amount of electricity deposited 22.0 g of silver from a solution of $AgNO_3$. How much copper will this same amount of current deposit from a solution of $CuSO_4$?

6. How many grams of nickel will be deposited from a solution of $NiSO_4$ by 40,000 coulombs of electricity?

7. How long would a current of 3.00 amp have to flow to deposit 50 g of copper from a solution of copper sulfate?

8. How many grams of nickel will be deposited from a solution of $NiCl_2$ by 4 amp of current flowing for 24 hr if the current efficiency is 96%?

CHAPTER 16

The Halogens

The practical everyday importance of the halogens, fluorine, chlorine, bromine, and iodine, and their compounds is indicated by the following facts:

The United States consumes annually about 17,000,000 tons of sodium chloride (NaCl, common salt). Common salt is so plentiful and so cheap that we are inclined to overlook the fact that it is an indispensable part of our daily diet. At the time of the Roman Empire it was so scarce and so highly prized that it constituted the major part of the Roman soldiers' pay; it was then known as "*sal*," and its use as payment for services rendered gave rise to the word "*salary*."

The United States produces about 2,750,000 tons of chlorine annually. The use of chlorine as a disinfectant for maintaining the purity of our drinking water is a major factor in the prevention of disease and contagion.

Tincture of iodine has long been one of our most widely used disinfectants. Radioactive iodine has relieved thousands of cases of hyperthyroidism. The beneficial effect of fluorides in prevention of tooth decay is becoming so well recognized that more and more communities are adding fluorine compounds to their drinking water supply. The entire photographic industry, including the movies and all other activities that involve the taking of pictures, is dependent upon the use of silver bromide.

16.1 Similarities and differences in the properties of the halogens (F_2, Cl_2, Br_2, and I_2). The study of the halogens, hydrogen halides (HF, HCl, HBr, and HI), and halide ions (F^-, Cl^-, Br^-, I^-) will be greatly simplified if the following facts about the halogens are kept in mind.

1. They all fall in group VIIA.
2. They all have 7 electrons in their valence shell.
3. The number of electron shells increases progressively by 1 as we go from F to Cl to Br to I. As the number of electron shells increases, the diameter of the atom increases.
4. The increase in atomic number of the halogen is accompanied by a

progressive increase in (a) atomic diameter, (b) density, (c) melting point, (d) boiling point (see Table 16.1).

In line with the fact that the halogens all fall in group VIIA and have 7 electrons in their valence shell:

1. They all have similar chemical properties.

2. They are all electronegative and are therefore classed as nonmetals. This is in line with the facts noted in Chapters 6 and 7 that: (a) the nonmetals fall in the right-hand section of the periodic table; (b) in any periodic period, as the atomic number increases, the electronegativity of the element increases.

3. They all show a strong tendency to combine with metals (electropositive elements) to form electrovalent binary compounds (salts). In this combination the halogen atom accepts one electron into its valence shell and becomes a monovalent anion (F^-, Cl^-, Br^-, I^-) whose valence is -1.

4. Two atoms of a given halogen combine with each other by the covalent sharing of a pair of electrons to form a diatomic molecule (F_2, Cl_2, Br_2, I_2).

5. One atom of halogen combines with 1 atom of hydrogen through the mutual sharing of a pair of electrons to form a covalent halide in which the halogen has an oxidation number of -1 (HF, HCl, HBr, HI).

6. They all show a tendency to combine with other nonmetals by mutual sharing of electrons to form covalent compounds (CCl_4, PI_3, $AsBr_3$, Cl_2O, SiF_4).

7. Solutions of their binary salts and binary acids all contain the monovalent negative halide ion (F^-, Cl^-, Br^-, I^-).

In comparing the chemical properties of the four halogens and their binary compounds it is important to keep in mind that:

1. Fluorine is the most electronegative (reactive), chlorine next, bromine next, and iodine the least: $F_2 > Cl_2 > Br_2 > I_2$.

2. In line with this order of electronegativity (reactivity) fluorides have the highest heats of formation, chlorides next, bromides next, and iodides the lowest.

3. The fluoride of a given element is most stable, the chloride next, the bromide next, and the iodide the least stable.

4. The electronegativity (reactivity) of the halogen decreases as (a) its atomic weight increases; (b) its atomic number increases; (c) its atomic diameter increases. This decrease in electronegativity with increase in atomic weight, atomic number, and atomic diameter may be accounted for as follows: When a halogen combines with another element it pulls an electron from that element into its valence shell and thereby acquires an inert gas structure. The pull on the electron is

TABLE 16.1

THE ELEMENTS OF GROUP VIIA

Element	Period	At. no.	At. wt	At. diam, Å	Electron configuration	Density	Mp	Bp	Color and state	Oxidation states
Fluorine	2	9	19.00	1.44	2, 7	1.78 g/l	−223.0°	−188.3°	colorless, gas	−1
Chlorine	3	17	35.457	1.99	2, 8, 7	3.214 g/l	−102°	−34.6°	greenish-yellow gas	−1, 1, 3, 5, 7
Bromine	4	35	79.916	2.28	2, 8, 18, 7	3.119 g/cc	−7.0°	58.0°	reddish-brown liquid	−1, 1, 5
Iodine	5	53	126.92	2.67	2, 8, 18, 18, 7	4.93 g/cc	sublimes	...	grayish-black solid	−1, 1, 5, 7
Astatine	6	85	(211)		2, 8, 18, 32, 18, 7					

exerted by the positive nucleus of the halogen atom. The greater the distance from the valence shell to this nucleus, the less strongly will the electron be attracted; that means that as the diameter increases in going from fluorine to chlorine to bromine to iodine, the valence shell is farther and farther from the nucleus, and the foreign electron is therefore less and less strongly attracted. It is true that, as the atomic number increases, the positive charge on the nucleus (atomic number) increases; this should increase the force with which the electron is attracted. However, to compensate for this increase in positive charge there is a corresponding increase in the number of electrons in the halogen structure; these electrons will *repel* the foreign electrons. The increase in diameter, that is, the increase in distance from the nucleus to the valence shell, would appear, therefore, to be the dominant factor that accounts for the decrease in electronegativity in going from fluorine to chlorine to bromine to iodine. Actually the whole picture is probably much more complex than that given above.

16.2 The properties of the hydrogen halides, HF, HCl, HBr, HI, and the ions, F^-, Cl^-, Br^-, and I^-

1. All four halides are covalent compounds with the structure

$$H\times\ddot{\underset{\cdot\cdot}{Cl}}:$$

2. The boiling points of HF, HCl, HBr, and HI are, respectively, 19.4°, −85°, −67°, and −35.5°. The increase in boiling point in going from HCl to HBr to HI is in line with the general rule that in a series of closely related covalently bonded compounds, the boiling point increases as the molecular weight increases. According to this rule HF should boil below −85°. Its abnormally high boiling point is due to its hydrogen bonding and strongly polar character; the highly dipolar HF molecules are so strongly attracted to each other that a relatively high temperature is required to vaporize them.

3. All four halides are colorless gases with almost identical sharp, penetrating, irritating odors.

4. Hydrofluoric acid, HF, has the highest heat of formation and is the most stable, HCl is next, HBr is next and, HI is the least stable; HI is endothermic—heat is absorbed when it is formed from H_2 and I_2. The order of stability of the halides is in line with the order of electronegativity of the halogens: the more electronegative the halogen, the more stable the halide.

5. All four halides are very soluble in water. Due to this high solubility they fume strongly in the presence of moist air. Thus if the moist breath is blown over the top of a tube from which one of the halides is

escaping, a heavy white cloud forms (this is an identification test); the HX dissolves in the moist breath to form a solution of acid which then condenses into a "fog."

6. As already noted above, the water solution of each halide is an acid. This is in line with the fact that the halogens are nonmetals, and nonmetals are acid-forming elements.

The halides HCl, HBr, and HI are strong acids; HF is weak. The weakly acid character of HF is in line with the small size of the fluorine atom and the F^- ion, and the consequent high stability of HF.

The following reaction takes place when each halide is dissolved in water.

$$HX + H_2O = H^+ \cdot H_2O + X^-$$

In solutions of HCl, HBr, and HI the predominant species are H^+ and Cl^-, Br^-, and I^-, respectively; in HF solution the predominant species is the HF molecule. Some association to form H_2F_2, H_3F_3, and H_6F_6 molecules is believed to occur.

Their water solutions, being acids, will show all the properties of acids listed in Section 13.1, page 253.

7. Solutions containing Cl^-, Br^-, and I^- ions, respectively, yield characteristic identifying precipitates when treated with a solution of a silver salt.

$$Ag^+ + Cl^- = AgCl \text{ (white)}$$
$$Ag^+ + Br^- = AgBr \text{ (cream color)}$$
$$Ag^+ + I^- = AgI \text{ (pale yellow)}$$

8. The gaseous halides all react with gaseous ammonia (NH_3) to form a white "cloud" of solid NH_4X; this is an excellent identification test.

$$NH_3 + HX = NH_4X \text{ (white salt)}$$

9. Hydrofluoric acid (gas or solution) will etch glass. This is a unique property characteristic only of HF. Glass is a complex material containing varying proportions of SiO_2, Na_2SiO_3 (sodium silicate), and $CaSiO_3$. The reactions with HF are

$$SiO_2 + 4\,HF = 2\,H_2O + SiF_4\uparrow$$
$$Na_2SiO_3 + 6\,HF = 2\,NaF + SiF_4\uparrow + 3\,H_2O$$
$$CaSiO_3 + 6\,HF = CaF_2 + SiF_4\uparrow + 3\,H_2O$$

This is the basis for the commercial use of HF for etching glassware.

10. The halides HCl, HBr, HI, and the ions Cl^-, Br^-, and I^- are reducing agents. Of these, HI and I^- are the strongest, while HCl and

Cl^- are the weakest. The more unstable the halide, the greater its reducing strength.

The reducing property of HX or the X^- ion can be demonstrated by treating it with an oxidizing agent such as solid $KClO_3$, MnO_2, or PbO_2. The following reactions typify what happens.

(1) $KClO_3 + 6\,HCl\ (conc) = KCl + 3\,H_2O + 3\,Cl_2\uparrow$

(2) $MnO_2 + 4\,HBr\ (conc) = MnBr_2 + 2\,H_2O + Br_2\uparrow$

(3) $PbO_2 + 4\,HI\ (conc) = PbI_2 + 2\,H_2O + I_2\uparrow$

(4) $MnO_2 + 2\,Cl^- + 4\,H^+ = Mn^{++} + 2\,H_2O + Cl_2\uparrow$

The halides HCl, HBr, and HI can be substituted for each other in each of these equations; the reactions will be the same as those given above.

If HCl gas is bubbled through concentrated H_2SO_4 no reaction takes place. If HBr gas is added to concentrated H_2SO_4 a mild reaction takes place; brown Br_2 gas and colorless SO_2 gas are liberated. The equation for the reaction is

(5) $$H_2SO_4 + 2\,HBr = H_2SO_3 + H_2O + Br_2\uparrow$$
$$H_2SO_3 = H_2O + SO_2\uparrow$$

If HI gas is added to concentrated H_2SO_4, a violent reaction takes place; solid I_2 is formed and H_2S gas is liberated. The equation for the reaction is

(6) $$H_2SO_4 + 8\,HI = H_2S + 4\,H_2O + 4\,I_2$$

An examination of the above equations brings out the following facts.

1. *The compounds* $KClO_3$, MnO_2, PbO_2, and H_2SO_4 *function as oxidizing agents.* This can be concluded from the fact that the oxidation number of a component element of each substance decreases; that means that the component element is reduced, and the compound which contains this element is the oxidizing agent. Thus in the reactions given above the oxidation number of Cl is reduced from +5 in $KClO_3$ to −1 in KCl, of Mn is reduced from +4 in MnO_2 to +2 in $MnBr_2$ and Mn^{++}, of Pb is reduced from +4 in PbO_2 to +2 in $PbCl_2$, of S is reduced from +6 in H_2SO_4 to +4 in H_2SO_3 and −2 in H_2S. Thus $KClO_3$, MnO_2, PbO_2, and H_2SO_4 can function as oxidizing agents because each contains, in a higher oxidation state, an element which can exist in compounds in a lower oxidation state.

2. The HCl, HBr, HI, and Cl^- *function as reducing agents* because they are responsible for the reduction in the oxidation number of the element (Cl, Mn, Pb, or S) that is reduced. That these substances are

reducing agents is indicated by the fact that one of their component elements (Cl, Br, or I) is oxidized. That the Cl, Br, and I are oxidized is shown by the fact that their oxidation numbers increase from -1 in HCl, HBr, HI, and Cl^- to 0 in the free halogen. Thus HCl, HBr, HI, and Cl^- illustrate the general rule that if a substance is to function as a reducing agent it must contain, in a lower oxidation state, an element that can exist in a higher oxidation state.

Hydriodic acid, HI, is a stronger reducing agent than HBr, which is a stronger reducing agent than HCl. This is shown by the fact that whereas HCl will not reduce H_2SO_4 at all, HBr will reduce it to H_2SO_3 in a mild reaction, while HI will reduce it to H_2S in a vigorous reaction.

3. These equations illustrate the general principle, stated in Section 4.4C, page 99, that *when, in a chemical reaction, one element is oxidized, that is, has its oxidation number increased, another element is reduced, that is, has its oxidation number decreased.*

4. *Free halogen is liberated when the hydrogen halide is oxidized.* Equation (2) represents the common laboratory method for preparing Cl_2, Br_2, and I_2.

5. *In the balanced equation the total increase in oxidation number of the element oxidized is equal to the total decrease in oxidation number of the element reduced.* Thus in equation (1), 1 atom of Cl has its oxidation number reduced from $+5$ in $KClO_3$ to -1 in KCl for a total decrease of 6; 6 atoms of chlorine have their oxidation number increased from -1 in HCl to O in Cl_2 for a total decrease of 6. In equations (2) and (4), 1 atom of Mn has its oxidation number reduced from $+4$ in MnO_2 to $+2$ in $MnCl_2$ or Mn^{++} for a total decrease of 2; 2 atoms of Cl have their oxidation number increased from -1 in HCl and Cl^- to 0 in Cl_2 for a total increase of 2. In equation (3), 1 atom of Pb has its oxidation number decreased from $+4$ in PbO_2 to $+2$ in $PbCl_2$ for a total decrease of 2; 2 atoms of chlorine have their oxidation number increased from -1 in HCl to 0 in Cl_2, for a total increase of 2. In equation (5), 1 atom of S has its oxidation number decreased from $+6$ in H_2SO_4 to $+4$ in H_2SO_3 for a decrease of 2; 2 atoms of Br have their oxidation number increased from -1 in HBr to 0 in Br_2 for a total increase of 2. In equation (6), 1 atom of S has its oxidation number decreased from $+6$ in H_2SO_4 to -2 in H_2S for a decrease of 8; 8 atoms of I each have their oxidation number increased from -1 in HI to 0 in I_2 for a total increase of 8.

6. *When a reaction involves ions, the net charges on the ions on the two sides of the balanced equation are equal.* Thus in reaction (4) the 2 Cl^- and 4 H^+ ions on the left side have a net charge of $+2$. The 1 Mn^{++} ion on the right also has a net charge of $+2$. This equality of net charges

is illustrated further by the following balanced oxidation-reduction equations:

(7) $2\,MnO_4^- + 10\,Cl^- + 16\,H^+ = 2\,Mn^{++} + 5\,Cl_2 + 8\,H_2O$

(8) $Cr_2O_7^{--} + 6\,Cl^- + 14\,H^+ = 2\,Cr^{+++} + 3\,Cl_2 + 7\,H_2O$

In equation (7) the net charge on the left is +4 (16^+, 10^-, and 2^-); the net charge on the right is also +4. In equation (8) the net charge on each side is +6.

16.3 Balancing oxidation-reduction equations by change in oxidation number. Since, as has been pointed out in Section 16.2, it is a fact that in any balanced equation: (*a*) *the total increase in oxidation number of the element oxidized is equal to the total decrease in oxidation number of the element reduced*, and (*b*) *the net charge on the ions must be the same on the two sides of the equation*, we can use these facts as an aid in balancing equations. To illustrate, suppose we want to balance the equation whose skeleton is represented by the expression

$$C + HNO_3 = CO_2 + NO_2 + H_2O$$

We note that the oxidation number of carbon changes from 0 in free carbon to +4 in CO_2. This means that carbon is oxidized. We note also that the oxidation number of nitrogen changes from +5 in HNO_3 to +4 in NO_2. This means that nitrogen is reduced. Since the oxidation number of carbon increases a total of 4 units, while the oxidation number of the nitrogen decreases by 1 unit, then, if the total increase in oxidation number of the element oxidized is going to equal the total decrease in oxidation number of the element reduced, 4 moles of HNO_3 will be required. We can then write the equation

$$1\,C + 4\,HNO_3 = 1\,CO_2 + 4\,NO_2 + H_2O$$

We note, by inspection, that we have 4 gram-atoms of hydrogen on the left side of the equation. Therefore we need 2 moles of H_2O on the right. The balanced equation is then

$$C + 4\,HNO_3 = CO_2 + 4\,NO_2 + 2\,H_2O$$

Suppose we wish to balance the equation whose skeleton we know to be

$$HNO_3 + P + H_2O = H_3PO_4 + NO$$

The oxidation number of phosphorus increases from 0 in P to +5 in H_3PO_4; phosphorus is oxidized. The oxidation number of nitrogen decreases from +5 in HNO_3 to +2 in NO; nitrogen is reduced. Since the

increase in oxidation number of P is 5, while the decrease in oxidation number of N is 3, we will need to select as the total change in oxidation number the least common multiple of 5 and 3, namely, 15. This will call for 3 gram-atoms of P (since the change per gram-atom of P is 5) and 5 gram-atoms of N (since the change per gram-atom of N is 3). We may thus write

$$5\ HNO_3 + 3\ P + (?)\ H_2O = 3\ H_3PO_4 + 5\ NO$$

To determine the amount of H_2O necessary, we simply note the number essential to balance the hydrogen. This gives the final balanced equation,

$$5\ HNO_3 + 3\ P + 2\ H_2O = 3\ H_3PO_4 + 5\ NO$$

The same technique can be used in balancing ionic equations; in this case, the net charges on the two sides of the equation must also be balanced. Thus to balance the equation

$$BiO_3^- + Mn^{++} = MnO_4^- + Bi^{+++}$$

we first note that the oxidation number of manganese has increased from +2 in Mn^{++} to +7 in MnO_4^-, while the oxidation number of bismuth has decreased from +5 in BiO_3^- to +3 in Bi^{+++}. Since the least common multiple of 5 and 2 is 10, we add the necessary coefficients to give

$$5\ BiO_3^- + 2\ Mn^{++} = 2\ MnO_4^- + 5\ Bi^{+++}$$

We find that the net charge on the left is −1 (−5 for the 5 BiO_3^- and +4 for the 2 Mn^{++}). The net charge on the right is +13 (+15 for the 5 Bi^{+++} and −2 for the 2 MnO_4^-). We can make the net charge the same on both sides by adding 14 H^+ to the left. The reaction is carried out in an acidic aqueous solution, so we have no trouble getting the necessary hydrogen ions. These 14 H^+ ions will yield 7 moles of H_2O. The balanced equation will then be

$$5\ BiO_3^- + 2\ Mn^{++} + 14\ H^+ = 2\ MnO_4^- + 5\ Bi^{+++} + 7\ H_2O$$

The equalization of the net charge in the above equation could have been accomplished by adding 14 OH^- ions to the right. These 14 OH^- ions on the right would have required the presence of 7 moles of H_2O on the left. The balanced equation would then be

$$5\ BiO_3^- + 2\ Mn^{++} + 7\ H_2O = 2\ MnO_4^- + 5\ Bi^{+++} + 14\ OH^-$$

As a general rule, the ions necessary to equalize the charge are *added to the left side:* H^+ ions if positive charges are needed, OH^- if negative charges are needed. Sometimes it is necessary to add the ion to the right side rather than to the left. Thus even though the left side may

have an excess of negative charges, one would not add H^+ ions to the left if the reaction is taking place in alkaline solution; such a solution would not contain a high enough concentration of H^+ ions to justify introducing them as reactants. In such a case OH^- ions would be added to the right. Likewise, one would not add OH^- ions to the left if the reaction took place in acid solution; H^+ ions would be added to the right.

In the following equation two elements are oxidized while one element is reduced.

$$As_2S_3 + NO_3^- = NO + H_3AsO_4 + SO_4^{--}$$

The oxidation number of N is decreased from +5 in NO_3^- to +2 in NO. Nitrogen is reduced; its oxidation number is decreased by 3 units. The oxidation number of As is increased from +3 in As_2S_3 to +5 in H_3AsO_4, and the oxidation number of sulfur is increased from −2 in As_2S_3 to +6 in SO_4^{--}; As and S are both oxidized. The oxidation number of As is increased by 2 units per gram-atom, for a total increase of 4 for each mole of As_2S_3. The oxidation number of S is increased by 8 units per gram-atom for a total increase of 24 for each mole of As_2S_3. Since As and S both are present in the same mole of As_2S_3, the total increase in oxidation number when *1 mole* of As_2S_3 reacts will be 28, or 4 for the 2 gram-atoms of arsenic and 24 for the 3 gram-atoms of sulfur. The least common multiple of 3, the decrease in oxidation number when the nitrogen in 1 NO_3^- is reduced to NO, and 28, the total increase in oxidation number when 1 mole of As_2S_3 reacts to form SO_4^{--} and H_3AsO_4, is 3×28. Hence we must take 3 moles of As_2S_3 and 28 moles of NO_3^-. This gives us

$$3\ As_2S_3 + 28\ NO_3^- = 28\ NO + 6\ H_3AsO_4 + 9\ SO_4^{--}$$

As the equation now stands, we have a total charge of −28 on the left and −18 on the right. To equalize the charges we must add 10 H^+ to the left. This gives us

$$3\ As_2S_3 + 28\ NO_3^- + 10\ H^+ = 28\ NO + 6\ H_3AsO_4 + 9\ SO_4^{--}$$

We notice that we have only 10 gram-atoms of hydrogen on the left, while there are 18 on the right. When the charges on the two sides of an equation have been equalized but more hydrogen is needed on one side, it must be added in the form of H_2O. So we will add 4 moles of H_2O to the left. This gives us the final balanced equation

$$3\ As_2S_3 + 28\ NO_3^- + 10\ H^+ + 4\ H_2O = 28\ NO + 6\ H_3AsO_4 + 9\ SO_4^{--}$$

As a final check on the balancing we note that there are 88 gram-atoms

When balancing by the oxidation number method it is necessary to recognize that many equations are a combination of both oxidation-reduction and double replacement. Thus when we try to balance the equation

$$Cu + HNO_3 = Cu(NO_3)_2 + H_2O + NO$$

we must modify our method slightly. The oxidation number of Cu increases from 0 to +2. The oxidation number of N decreases from +5 to +2. The least common multiple of +2 and −3 is 6. Hence we would expect to take 3 Cu and 2 HNO_3. This would give

$$3\ Cu + 2\ HNO_3 = 3\ Cu(NO_3)_2 + H_2O + 2\ NO$$

which is certainly not balanced. If we re-examine this equation we notice that nitrate appears on the right side of the equation, a total of 6 nitrate radicals in fact. That means that 2 moles of HNO_3 were reduced to NO, while 6 moles of HNO_3 reacted, without being reduced, to form 3 $Cu(NO_3)_2$. Therefore a total of 8 moles of HNO_3 must have reacted. Readjusting the number of moles of H_2O to take care of the changed value for HNO_3 gives us

$$3\ Cu + 8\ HNO_3 = 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO$$

In reactions of this kind, where it is obvious that some of the oxidant is reduced, while some of it takes part in an ordinary double replacement reaction, it is a good policy to add the required coefficients to the *right side of the equation first* and then work back to the left side. Had we done that in the above equation we would have obtained

$$Cu + HNO_3 = 3\ Cu(NO_3)_2 + 2\ NO$$

as our first adjustment. Next we would adjust the number of gram-atoms of copper to 3. Then, having observed that we have a total of 6 nitrates and 2 moles of NO on the right, we would know that 8 moles of HNO_3 would be needed to give the required number of gram-atoms of N. These 8 moles of HNO_3 would yield 4 moles of H_2O.

When a diatomic molecule such as Cl_2, I_2, Br_2, O_2, H_2, or N_2 is involved in a process of oxidation or reduction, it is important to recognize that no less than 2 gram-atoms of the substance involved must appear on each side of the equation. In such a situation we determine first the change in oxidation number for 2 gram-atoms (1 mole) of the gas, and use this value in determining the least common multiple of the increase and decrease in oxidation number. Thus in balancing the equation

$$HNO_2 + I^- = NO + I_2$$

we must determine the increase in oxidation number for *2 gram-atoms* (1 mole) of iodine, since we can have nothing less than 1 mole of I_2 on the right. The skeleton of the equation is, in reality

$$HNO_2 + 2\,I^- = NO + I_2$$

The decrease in oxidation number of the N is 1; the increase for the *2* gram-atoms of I is 2. The balanced equation will therefore be

$$2\,HNO_2 + 2\,I^- + 2\,H^+ = 2\,NO + I_2 + 2\,H_2O$$

When balancing an equation of the type

$$S + SO_4^{--} = SO_2$$

it should be noted that the SO_2 in the product is formed in part from S, by oxidation to SO_2, and in part from SO_4^{--}, by reduction to SO_2. One should then write, or think, the skeleton of the equation in such a way as to designate that the SO_2 is derived from two sources.

$$\mathbf{S} + SO_4^{--} = \mathbf{SO_2} + SO_2$$

The boldface S has its oxidation number *increased* from 0 to 4, whereas the other S has its oxidation number *decreased* from 6 to 4. Balancing as noted above gives

$$\mathbf{S} + 2\,SO_4^{--} = \mathbf{SO_2} + 2\,SO_2$$

The final equation is then

$$S + 2\,SO_4^{--} + 4\,H^+ = 3\,SO_2 + 2\,H_2O$$

The same thing should be noted in balancing the following equations:

$$Cl_2 + OH^- = Cl^- + ClO_3^-$$
$$KClO_3 = KCl + KClO_4$$

When H_2O_2 appears as an oxidant in a reaction such as

$$Cr(OH)_4^- + H_2O_2 = CrO_4^{--} + H_2O$$

one faces a compound, H_2O_2, made up of two elements, H and O, whose oxidation numbers have been arbitrarily defined as $+1$ and -2, respectively. Because hydrogen is the reference element in the assignment of oxidation numbers, it has its usual oxidation number of $+1$. That means that, in this compound, the oxidation number of each of the two oxygen atoms in H_2O_2 is -1. The 2 atoms of oxygen in the H_2O_2 molecule together have an oxidation number of -2. In the products CrO_4^{--} and H_2O oxygen has its normal oxidation number of -2. Therefore the total decrease in the oxidation number of the 2 gram-atoms of oxygen

per mole of H_2O_2 is 2. The oxidation number of chromium is increased from +3 in $Cr(OH)_4^-$ to +6 in CrO_4^{--}. The least common multiple of 2 and 3 is 6, so we get

$$2\ Cr(OH)_4^- + 3\ H_2O_2 = 2\ CrO_4^{--} + ?\ H_2O$$

To equalize the charge on the two sides of the equation we must add 2 OH^- to the left. The reaction is carried out in alkaline solution, so the addition of OH^- ions at the left is proper. This gives us a total of 16 gram-atoms of hydrogen on the left. Therefore we will need 8 H_2O on the right. The balanced equation is then

$$2\ Cr(OH)_4^- + 3\ H_2O_2 + 2\ OH^- = 2\ CrO_4^{--} + 8\ H_2O$$

16.4 Laboratory preparation of HF, HCl, HBr, and HI

1. *Preparation of* HF *and* HCl, *by the reaction of concentrated* H_2SO_4 *on a metal halide*

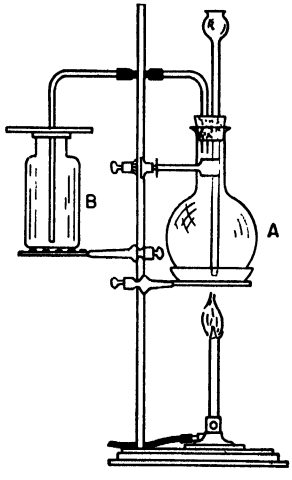


Figure 16.1. Laboratory preparation of HCl gas. Solid NaCl is placed in flask *A*. Concentrated sulfuric acid is added through the thistle tube. The HCl gas is collected in bottle *B* by displacement of the air in the bottle. The reaction is always carried out under a hood because of the sharp, irritating odor and corrosive character of HCl gas.

$$CaF_2 + H_2SO_4\ (\text{heated}) = CaSO_4 + 2\ HF$$

$$NaCl + H_2SO_4\ (\text{heated}) = NaHSO_4 + HCl$$

This illustrates the general method, salt + nonvolatile acid = new salt + new acid, discussed in Section 13.4. The hydrogen halides are very soluble in water and are more dense than air. They are therefore collected by upward displacement of air (see Figure 16.1). Pure HBr and HI cannot be prepared by this method; they are such strong reducing agents that they reduce H_2SO_4 to H_2SO_3 and H_2S, respectively, in the manner discussed in Section 16.2, free Br_2 and I_2 being liberated in the reaction.

2. *Preparation of* HBr *and* HI, *by hydrolysis of* PBr_3 *and* PI_3, respectively (see 13.4).

$$PBr_3 + 3\ H_2O = H_3PO_3 + 3\ HBr\uparrow$$

$$PI_3 + 3\ H_2O = H_3PO_3 + 3\ HI\uparrow$$

16.5 Commercial preparation of HF, HCl, HBr, and HI

1. *Preparation of* HF by the action of concentrated H_2SO_4 on fluorspar (CaF_2)

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

2. *Preparation of* HCl

(a) By the action of concentrated H_2SO_4 on common salt

$$NaCl + H_2SO_4 = NaHSO_4 + HCl\uparrow$$
$$NaHSO_4 + NaCl\ (\text{heated}) = Na_2SO_4 + HCl\uparrow$$

(b) By burning hydrogen in an atmosphere of chlorine

$$H_2 + Cl_2 = 2\,HCl$$

3. *Preparation of* HBr *and* HI by the hydrolysis of the phosphorus halides (see 16.4)

16.6 Some important commercial uses of the hydrohalogen acids

1. *Hydrofluoric acid*

(a) As a catalyst in the synthesis of a number of organic compounds

(b) As a reactant in the synthesis of gasoline and plastics

(c) Etching of glassware (see 16.2)

2. *Hydrochloric acid*

(a) "Pickling" of metals (removing the film or "scale" of metal oxide)

$$Fe_2O_3 + 6\,H^+ + 6\,Cl^- = 2\,Fe^{+++} + 6\,Cl^- + 3\,H_2O$$
$$CuO + 2\,H^+ + 2\,Cl^- = Cu^{++} + 2\,Cl^- + H_2O$$

(b) Neutralization of excess base and carbonate in various industrial processes

$$OH^- + H^+ + Cl^- = H_2O + Cl^-$$
$$CO_3^{--} + 2\,H^+ + 2\,Cl^- = H_2O + CO_2\uparrow + 2\,Cl^-$$

(c) Synthesis of organic compounds

(d) Commercial preparation of chlorides of metals

$$MgO + 2\,H^+ + 2\,Cl^- = Mg^{++} + 2\,Cl^- + H_2O$$

(e) Numerous other uses that are dependent upon its acid and reducing properties

3. *Hydrobromic and hydriodic acids.* Limited use in synthesis of organic compounds

16.7 Laboratory preparation of Cl_2, Br_2, and I_2

1. *All three are prepared by oxidation of the hydrogen halide* (sec 16.2).

$$(O) \text{ (from oxidizing agent)} + 2\,HX = H_2O + X_2$$

Manganese dioxide is the oxidizing agent most commonly used.

$$MnO_2 + 4\,H^+ + 2\,Cl^- = Mn^{++} + 2\,H_2O + Cl_2\uparrow$$

A mixture of MnO_2 and the halide of a metal is commonly treated with concentrated H_2SO_4. The halide probably first reacts with the H_2SO_4 to form HCl, which is immediately oxidized by the MnO_2. The over-all equation is

$$MnO_2 + 2\,NaBr + 2H_2SO_4\,(conc) = MnSO_4 + Na_2SO_4 + 2\,H_2O + Br_2\uparrow$$

2. *Bromine and iodine can be prepared by replacement* from solutions of their salts by the more active element, chlorine.

$$Cl_2 + 2\,Br^- = 2\,Cl^- + Br_2$$
$$Cl_2 + 2\,I^- = 2\,Cl^- + I_2$$

3. Because of its high reactivity and the consequent low reducing power of HF and F^-, fluorine cannot be prepared by the above methods. Because of its corrosiveness, fluorine is normally not prepared in the laboratory.

16.8 Commercial preparation of the halogens

1. *Fluorine.* By electrolysis of a solution of KF in liquid HF contained in a copper cell and using pure graphite electrodes. Fluorine is liberated at the positive pole and hydrogen at the negative. The liquid HF is an excellent dissociating solvent; therefore the solution contains H^+, K^+, and F^- ions and HF molecules. It is believed that, during electrolysis, the F^- ions are attracted to the positive pole, where they give up an electron and escape as F_2 gas, while the H^+ ions migrate to the negative pole, pick up an electron, and escape as H_2 gas.

2. *Chlorine.* By electrolysis of a brine solution (NaCl in water) in the manner discussed in Section 15.2. A relatively small amount is obtained by electrolysis of melted NaCl as discussed in Section 15.1.

3. *Bromine.* By replacement by chlorine from the bromine salt. In the United States these salts are obtained from the natural brines pumped from deep wells in Michigan. Increasing amounts of bromine are recovered each year from the bromides present in sea water.

4. *Iodine.* Largely from the Chile saltpeter ($NaNO_3$) deposits where it occurs as sodium iodate ($NaIO_3$). It is recovered by reduction of the iodate solution with sodium hydrogen sulfite ($NaHSO_3$).

$$2\,IO_3^- + 5\,HSO_3^- = 5\,SO_4^{--} + 3\,H^+ + H_2O + I_2$$

Some iodine is recovered from California salt brines by replacement by chlorine.

$$Cl_2 + 2\,I^- = 2\,Cl^- + I_2$$

16.9 Properties of the halogens (see also 16.1 and Table 16.1).

1. *They combine with all metals to form stable halides* (salts). The more electronegative the halogen, the more vigorous the reaction, the greater the heat of formation of the halide, the more stable the halide.

$$2\,K + F_2 = 2\,KF + 118{,}100 \text{ cal/mole}$$

The heats of formation of KCl, KBr, and KI are 104,300, 95,100, and 80,100 cal/mole, respectively.

When metals such as Fe, Sn, and Hg, which commonly exist in their binary compounds in two oxidation states, combine with a halogen they take the higher oxidation state. This illustrates the rule that *in the presence of a strong oxidizing agent a polyvalent element takes a high oxidation state.*

$$2\,Fe + 3\,Cl_2 = 2\,FeCl_3$$
$$Sn + 2\,Cl_2 = SnCl_4$$

In contrast, when Fe and Sn are treated with HCl, the salts $FeCl_2$ and $SnCl_2$ are recovered when the solutions are evaporated to dryness. In this instance the salt is formed in the presence of a reducing agent (H) and the metal tends, accordingly, to take a low oxidation state.

$$Fe + 2\,H^+ + 2\,Cl^- = Fe^{++} + 2\,Cl^- + H_2\uparrow$$
$$Sn + 2\,H^+ + 2\,Cl^- = Sn^{++} + 2\,Cl^- + H_2\uparrow$$

2. *They combine with nonmetals to form covalent halides.*

$$2\,P + 5\,Cl_2 = 2\,PCl_5$$
$$Si + 2\,Cl_2 = SiCl_4$$

3. *They combine with hydrogen to form the hydrogen halide.* As noted earlier, the more electronegative the halogen, the more vigorous the reaction, the greater the heat of formation, and the more stable the halide. The heats of formation are: HF, 38,600 cal/mole; HCl, 22,000 cal/mole; HBr, 8,400 cal/mole; HI, −6,000 cal/mole.

4. *They all react with water.*

(a) Because of its great electronegativity, F_2 reacts violently with cold water.

$$2\,F_2 + 2\,H_2O = 4\,HF + O_2\uparrow$$

(b) The halogens Cl_2, Br_2, and I_2 react with cold water to form hydrohalic (HCl, HBr, HI) and hypohalous (HOCl, HOBr, HOI) acids.

$$Cl_2 + H_2O \rightleftarrows H^+ + Cl^- + HOCl$$
$$Br_2 + H_2O \rightleftarrows H^+ + Br^- + HOBr$$
$$I_2 + H_2O \rightleftarrows H^+ + I^- + HOI$$

The solubilities of Cl_2, Br_2, and I_2 in grams per 100 g of water at 25° are 0.63, 3.3, and 0.03, respectively. The solutions owe their characteristic colors and odors to the free halogen that is present.

The hypohalous acids HOCl, HOBr, and HOI are strong oxidizing agents. Therefore water solutions of the halogens are good oxidizing agents. It is this property of chlorine water that is the basis for its use in the purification of water and as a bleaching agent; it oxidizes the impurities and colored materials. It cannot bleach nonoxidizable material such as iron rust (Fe_2O_3).

5. *They all react with solutions of strong bases.* This would be expected from the fact that their water solutions contain free acid in equilibrium with the free halogen. The detailed equations for the reaction of bromine with a solution of NaOH probably are:

(1) $Br_2 + H_2O \rightleftarrows H^+ + Br^- + HOBr$

(2) $NaOH \rightarrow Na^+ + OH^-$

(3) $H^+ + OH^- = H_2O$

(4) $HOBr + OH^- = H_2O + OBr^-$

The net equation for the reaction is

(5) $Br_2 + 2\,OH^- = Br^- + OBr^- + H_2O$

That equation (1) is an incomplete reaction which reaches a state of equilibrium is indicated by the following behavior: When NaOH is added to a brown solution of bromine in water, the brown color disappears. This is accounted for by equations (2), (3), and (4), which remove H^+ and HOBr from equation (1) and cause it to be complete to the right.

If H_2SO_4 (or some other acid) is added to the colorless solution, the brown color reappears. This is accounted for by the following reactions:

(6) $2\,H^+$ (from H_2SO_4) $+ Br^- + OBr^- = H^+ + Br^- + HOBr$

(7) $H^+ + Br^- + HOBr \rightleftarrows H_2O + Br_2$ (brown)

Note that reactions (7) and (1) are the same. The test of a true equilibrium is that it can be attained by starting with either the reactants on the left or those on the right. In this instance we attain the same

equilibrium condition whether we start with Br_2 and H_2O or H^+, Br^-, and HOBr.

6. *A more electronegative halogen replaces a less electronegative one from its binary compounds.*

$$Cl_2 + CaI_2 = CaCl_2 + I_2\uparrow$$
$$Cl_2 + 2\,Br^- = 2\,Cl^- + Br_2$$

This serves as an identification test for chlorine and a method for preparing Br_2 and I_2.

7. *They all react with a great many different organic compounds* to form a variety of products. This property will be considered in more detail in Chapter 22.

CH_4 (methane) + Cl_2 = CH_3Cl (methyl chloride) + HCl

$C_{10}H_{16}$ (turpentine) + 8 Cl_2 (heated) = 10 C + 16 HCl

C_2H_4 (ethylene) + Br_2 = $C_2H_4Br_2$ (ethylene bromide)

8. *Iodine reacts with iodide ion to form the soluble complex ion* I_3^-. As a consequence, iodine is very soluble in solutions of KI and NaI. These compounds are used as solubleizing agents in preparing solutions of iodine in water.

$$I_2 + I^- \rightleftarrows I_3^-$$

9. *Iodine reacts with starch to give a deep blue starch-iodine product.* This serves as an excellent identification test for free iodine. The iodide ion does not give this test.

$$\text{starch} + I_2 \rightleftarrows \text{starch-}I_2 \text{ complex (blue)}$$

10. *Iodine oxidizes thiosulfate ion* ($S_2O_3^{--}$) *to the tetrathionate ion* ($S_4O_6^{--}$).

$$2\,S_2O_3^{--} + I_2 = S_4O_6^{--} + 2\,I^-$$

This reaction is specific for iodine, and serves for its quantitative determination. Starch can be used as an indicator in this titration; the blue starch-I_2 color disappears the moment all the iodine has reacted with $S_2O_3^{--}$.

11. Iodine sublimes when heated (see 2.22).

12. Iodine is more soluble in carbon tetrachloride (CCl_4), ether [$(C_2H_5)_2O$], and kerosene (a mixture of hydrocarbon compounds) than it is in water. Since these three substances are insoluble in water, they can be used for extracting iodine from its water solution (see 11.9).

16.10 Some important commercial uses of the halogens

1. *Fluorine.* Manufacture of Freon (CCl_2F_2 and $C_2Cl_2F_4$) for use as a refrigerant; manufacture of plastics.

2. *Chlorine.* Manufacture of chlorinated organic compounds (CH_3Cl, CCl_2F_2, $C_2Cl_2F_4$, $CHCl_3$, CCl_4, etc.; see 16.9–7); manufacture of Br_2, I_2, and HCl (see 16.9–6 and 16.5); bleaching of textiles, wood pulp, and paper (see 16.9–4); water purification (see 16.9–4); detinning tin cans and tin plate (see 16.9–1).

3. *Bromine.* Manufacture of ethylene bromide ($C_2H_4Br_2$) for use as a component of "ethyl" gasoline (see 16.9–7); manufacture of AgBr for use in photography (see 16.2–7); manufacture of dyes and organic chemicals (see 16.9–7).

4. *Iodine.* Manufacture of KI and NaI; manufacture of dyes and organic chemicals; manufacture of AgI for use in photography; tincture of iodine (solution of iodine in ethyl alcohol) for use as an antiseptic.

16.11 Oxygen compounds of the halogens. Chlorine, bromine, and iodine form a number of important and interesting oxides and ternary oxygen compounds. They will not, however, be given detailed treatment in this book. When they are encountered, as has already happened with $KClO_3$, HOBr, HOCl, and HOI, it will be noted that they are oxidizing agents in which the halogens have positive oxidation numbers. The various binary and ternary halogen compounds illustrate a rule, which applies to all the nonmetals in groups IIIA, IVA, VA, VIA, and VIIA, that the element tends to take its lowest (negative) oxidation state in its hydrogen halide and binary salts and the higher (positive) oxidation state in its compounds (oxides and ternary oxygen compounds) with the strongly electronegative nonmetal oxygen. Fluorine provides the exception to the latter part of the rule; because it is more electronegative than oxygen, it has a negative oxidation state in its oxide, the oxidation state of the oxygen being therefore positive. The maximum oxidation number of a halogen is +7 ($HClO_4$). When we complete our study of the elements in groups IIIA, IVA, VA, VIA, and VIIA, we will have learned that the maximum oxidation numbers of the elements in these groups are, with a few exceptions, respectively, +3, +4, +5, +6, and +7.

16.12 Equivalent weights of compounds used in oxidation-reduction reactions. When hydrogen gas is passed over heated $KClO_3$ the following oxidation-reduction reaction takes place.

$$KClO_3 + 3\ H_2 = KCl + 3\ H_2O$$

Potassium chlorate is the oxidizing agent; hydrogen is the reducing agent. Since 1 mole of $KClO_3$ reacts with 6 gram-atoms of hydrogen, it follows that 1 mole of $KClO_3$ is equivalent to 6 gram-atoms of hydrogen, and $\frac{1}{6}$ mole of $KClO_3$ is equivalent to 1 gram-atom of hydrogen. The equivalent weight has been defined

as that weight of a substance which is equivalent to (will react with or replace) 1 gram-atom of hydrogen. That means that the equivalent weight of $KClO_3$ is, in this particular reaction, equal to $\frac{1}{6}$ its formula weight. The oxidation number of chlorine is +5 in $KClO_3$ and −1 in KCl. That means that in the course of this reaction, the oxidation number of chlorine has decreased by a total of 6 units (+5 to −1). We note then that in this reaction the oxidation number of the chlorine has decreased by 6, and the equivalent weight of the $KClO_3$ is one-sixth its formula weight.

When hydrogen gas is passed over heated $KClO_4$, the following oxidation-reduction reaction takes place:

$$KClO_4 + 4\,H_2 = KCl + 4\,H_2O$$

where $KClO_4$ is the oxidizing agent, and hydrogen is the reducing agent. In this reaction 1 mole of $KClO_4$ reacts with 8 gram-atoms of hydrogen. Therefore 1 gram-atom of hydrogen is equivalent to $\frac{1}{8}$ mole of $KClO_4$. That means that the equivalent weight of $KClO_4$ is one-eighth its formula weight. The oxidation number of chlorine decreases from +7 in $KClO_4$ to −1 in KCl, a total decrease of 8. We note then, that in this reaction the oxidation number of the chlorine has decreased by 8 and the equivalent weight of $KClO_4$ is one-eighth its formula weight.

If solid sodium sulfite is heated with oxygen gas, the following oxidation-reduction reaction takes place:

$$2\,Na_2SO_3 + O_2 = 2\,Na_2SO_4$$

where Na_2SO_3 is the reducing agent, and O_2 is the oxidizing agent. In this reaction 1 mole of Na_2SO_3 is equivalent to 1 gram-atom of oxygen. One-half mole of Na_2SO_3 is therefore equivalent to $\frac{1}{2}$ gram-atom of oxygen. The equivalent weight has already been defined as that weight of a substance which is equivalent to 1 gram-atom of hydrogen, or $\frac{1}{2}$ gram-atom of oxygen. Therefore the equivalent weight of Na_2SO_3 in this reaction is one-half its formula weight. The oxidation number of sulfur has increased in this reaction from +4 in Na_2SO_3 to +6 in Na_2SO_4, a total increase of 2. We note again that in this reaction the oxidation number of the sulfur has increased by 2, and the equivalent weight of Na_2SO_3 is one-half its formula weight.

When oxygen gas is passed into a solution containing tetrahydroxostannate(II) ions, $Sn(OH)_4^{--}$, the following oxidation-reduction reaction takes place:

$$2\,Sn(OH)_4^{--} + O_2 + 2\,H_2O = 2\,Sn(OH)_6^{--}$$

Stannate(II) ions are the reducing agent, oxygen is the oxidizing agent. One gram-ion of $Sn(OH)_4^{--}$ is equivalent to 1 gram-atom of oxygen; $\frac{1}{2}$ gram-ion of $Sn(OH)_4^{--}$ is equivalent to $\frac{1}{2}$ gram-atom of oxygen. Therefore the equivalent weight of the $Sn(OH)_4^{--}$ ion is one-half its gram-ion weight. The oxidation number of tin has increased from +2 in $Sn(OH)_4^{--}$ to +4 in $Sn(OH)_6^{--}$, a total increase of 2. Here again we note that the oxidation number of the tin has increased by 2, and the equivalent weight of $Sn(OH)_4^{--}$ is one-half its gram-ion weight.

From these and many similar cases we arrive at the following rule: The equivalent weight of a compound or ion in an oxidation-reduction reaction is equal to the formula weight or gram-ion weight divided by the change in oxidation number of the element oxidized or reduced. In a reaction in which $KMnO_4$ (or MnO_4^-) is reduced to Mn^{++}, the oxidation number change of the Mn is 5; therefore the equivalent weight of $KMnO_4$ is one-fifth its formula weight. In a reaction in which $KMnO_4$ is reduced to MnO_2, the oxidation number change of the Mn is 3; therefore the equivalent weight of $KMnO_4$ is one-third its formula weight. In a reaction in which $Cr_2O_7^{--}$ is reduced to 2 Cr^{+++}, the total oxidation number change for the 2 gram-atoms of chromium in a mole of $K_2Cr_2O_7$ is 6; therefore the equivalent weight of the $K_2Cr_2O_7$ is one-sixth its formula weight. In a reaction in which Fe^{++}, as $FeSO_4$, is oxidized to Fe^{+++}, the oxidation number change of the iron is 1; therefore the equivalent weight of $FeSO_4$ is equal to its formula weight.

The rule about number of equivalent weights of reactants already stated for double decomposition and replacement reactions also applies to oxidation-reduction reactions. That is, in any reaction the number of equivalent weights of oxidizing agent equals the number of equivalent weights of reducing agent.

It is obvious from what has been stated, that in preparing or working with a solution of specific normality, one must know whether the reaction in which the solute is to be used involves double decomposition, complex ion formation, or oxidation-reduction. In each instance the exact formulas of the ions and molecules involved must be known.

To illustrate, suppose we are asked to prepare 400 ml of a 0.1 normal solution of $KMnO_4$ for use in titrating an acidic solution of Fe^{++}. The reaction that will take place is

$$MnO_4^- + 5\,Fe^{++} + 8\,H^+ = Mn^{++} + 5\,Fe^{+++} + 4\,H_2O$$

The change in oxidation number per gram-ion of MnO_4^- (mole of $KmnO_4$) is 5. Therefore 1 gram-equivalent weight of $KMnO_4$ will be 0.2 mole. That will be 0.2×158 g (the gram-formula weight of $KMnO_4$), or 31.6 g. Since we are to prepare a 0.1 *N* solution, we will need 0.1×31.6 g, or 3.16 g, of $KMnO_4$ per liter of solution. Since we are to prepare only 400 ml (0.4 l), we will need 0.4×3.16 g, or 1.26 g.

Questions and Problems

1. Arrange the four halogens in the order of increasing: (a) atomic number; (b) atomic weight; (c) atomic diameter; (d) density; (e) melting point; (f) boiling point; (g) depth of dark color; (h) number of electrons; (i) number of valence electrons; (j) reactivity; (k) electronegativity; (l) strength as oxidizing agents. Account for the order given in (j), (k), and (l).

2. Arrange the four hydrogen halides in the order of increasing: (a) density; (b) molecular weight; (c) boiling point; (d) heat of forma-

tion; (e) stability; (f) strength as reducing agents. Account for the order given in (e) and (f).

3. In each horizontal line circle the substance which qualifies for the classification listed on the left.

Highest atomic number	F	Cl	Br	I
Highest atomic weight	F	Cl	Br	I
Highest melting point	F	Cl	Br	I
Highest boiling point	F	Cl	Br	I
Most reactive	F	Cl	Br	I
Most electronegative	F	Cl	Br	I
Most electropositive	F	Cl	Br	I
Strongest oxidizing agent	F	Cl	Br	I
Most stable	HF	HCl	HBr	HI
Strongest reducing agent	HF	HCl	HBr	HI
Highest boiling point	HF	HCl	HBr	HI
Lowest boiling point	HF	HCl	HBr	HI
Weakest acid	0.1 *M* HF	0.1 *M* HCl	0.1 *M* HBr	0.1 *M* HI
Poorest electric conductor	0.1 *M* HF	0.1 *M* HCl	0.1 *M* HBr	0.1 *M* HI
Lowest hydrogen ion concentration	0.1 *M* HF	0.1 *M* HCl	0.1 *M* HBr	0.1 *M* HI
Smallest ionization constant	0.1 *M* HF	0.1 *M* HCl	0.1 *M* HBr	0.1 *M* HI
Highest *p*H	0.1 *M* HF	0.1 *M* HCl	0.1 *M* HBr	0.1 *M* HI
Highest hydroxyl ion concentration	0.1 *M* HF	0.1 *M* HCl	0.1 *M* HBr	0.1 *M* HI
Strongest reducing agent	0.1 *M* F^-	0.1 *M* Cl^-	0.1 *M* Br^-	0.1 *M* I^-
Most strongly hydrolyzed	0.1 *M* F^-	0.1 *M* Cl^-	0.1 *M* Br^-	0.1 *M* I^-
Highest *p*H	1 *M* NaF	1 *M* NaCl	1 *M* NaBr	1 *M* NaI
Highest boiling point	CH_3F	CH_3Cl	CH_3Br	CH_3I

4. Give the orbital arrangement of all electrons (*s*, *p*, *d*, and *f*) in the atoms of F, Cl, Br, and I. Point out the similarities and differences in the structure of the atoms of F, Cl, Br, and I. What significance attaches to their similarities? To their differences?

5. How could you demonstrate, using all available tests, that a solution of HBr in water is an acid? Write net equations for all reactions that take place.

6. How could you demonstrate, using all available methods, that HCl is a stronger acid than HF? Write net equations for all reactions that take place.

7. Starting with a solution of HCl as the only source of chlorine,

and any other materials that you need, write equations for all methods that could be used for preparing $MgCl_2$.

8. Describe a series of experiments by means of which you could show: (a) that HCl, HBr and HI are reducing agents; (b) that HBr and HI are stronger reducing agents than HCl; (c) that HI is a stronger reducing agent than HBr. Write net equations for all reactions that take place.

9. Describe a series of experiments which would show that chlorine is more electronegative than bromine and iodine and that bromine is more electronegative than iodine. Write net equations for all reactions.

10. You are given only the following: a source of heat, Na, Mg, S, NaCl, Fe, concentrated H_2SO_4, dilute H_2SO_4, $KClO_3$ (water and air are not to be used). Show, by a series of balanced chemical equations how each of the following could be formed, $MgSO_3$; $FeCl_2$; $FeCl_3$; NaClO.

11. The following solid oxidizing agents are all able to oxidize HCl, HBr, and HI: MnO_2, PbO_2, $CaCl_2O$, $KClO_3$, $KMnO_4$, $K_2Cr_2O_7$. Write net equations for the reaction of HCl, HBr, and HI with each one. Select one of the balanced equations and point out: (a) the element oxidized; (b) the element reduced; (c) the total oxidation number increase of the oxidized element; (d) the total oxidation number decrease of the element reduced; (e) the reducing agent; (f) the oxidizing agent.

12. Arrange the following in the order of their increasing *p*H: (a) 0.1 *M* HF; (b) 0.1 *M* NaCl; (c) 0.1 *M* NaF; (d) 0.1 *M* NH_4Cl; (e) 0.1 *M* NH_4F; (f) 0.1 *M* HCl.

13. How could you distinguish between four liquids, one H_2O, one dilute HF, one dilute HCl, one dilute HI?

14. How could you distinguish, by physical or chemical methods, between four colorless gases, one HCl, one H_2, one O_2, and one air?

15. How could you distinguish between seven solids, one NaF, one NaCl, one NaBr, one NaI, one Na_2CO_3, one Na_2SO_4, one $CaCl_2O$?

16. Tin yields $SnCl_2$ when treated with HCl, but yields $SnCl_4$ when treated with Cl_2. Explain.

17. Account for the statement, "the halogens are oxidizing agents."

18. What is meant by the statement, "the halogens are strongly electronegative"?

19. How could you distinguish, by chemical tests, between the two substances in each of the following pairs? (a) MnO_2 and CuO, black solids; (b) $KClO_3$ and KCl, white solids; (c) 1 *M* NaCl and 1 *M* NaI;

(d) KI and KBr, solids; (e) KCl and KBr, solids; (f) Ni and Ag, solids; (g) Na_2CO_3 and NaCl, solids; (h) solutions of Br_2 and I_2.

20. What is the oxidation number of Cl in each of the following covalent compounds: HCl; HClO; $HClO_2$; $HClO_3$; $HClO_4$? Keeping in mind that, when added to water, these covalent compounds yield hydrogen ions (hydronium ions) and Cl^-, OCl^-, $OClO^-$ (ClO_2^-), $OClO_2^-$ (ClO_3^-) and $OClO_3^-$ (ClO_4^-) ions, respectively, sketch each of the above covalent (un-ionized) molecules, showing how the atoms are arranged and what types of valence bonds are involved.

21. Show, by net equations, how chlorine gas reacts with each of the following: (a) a heated metal; (b) a heated nonmetal; (c) heated hydrogen; (d) cold water; (e) a cold solution of KOH; (f) a solution of KBr.

22. When NaOH is added to a brown solution of bromine in water the brown color disappears. When dilute H_2SO_4 is added to the colorless solution, the brown color reappears. Explain, giving equations for all reactions.

23. You are given a solution of iodine in water in which the following reaction is taking place: $I_2 + H_2O \rightleftarrows H^+ + I^- + HIO$. How will the equilibrium point in this reaction be affected by the following: (a) addition of $Na_2S_2O_3$; (b) addition of NaOH; (c) addition of KI; (d) addition of some reducing agent, such as H_2SO_3; (e) addition of HI; (f) addition of $AgNO_3$.

24. How could you demonstrate that a solution of iodine in water also contains I^- ions in the form of a soluble iodide?

25. How could you demonstrate that a brown solution of Br_2 contains some dissolved iodine?

26. How could you demonstrate that a solution of a metal chloride contains also some iodide?

27. How could you demonstrate that chlorine is a nonmetal?

28. Write net equations for the reactions that take place in each of the following:

(a) Magnesium is burned in an atmosphere of I_2 gas.
(b) Phosphorus is burned in bromine gas.
(c) Chlorine is added to a solution of KOH.
(d) A moist substance is bleached with chlorine.
(e) Sulfur dioxide gas is passed into a solution of iodine in water.
(f) Silver nitrate solution is added to a solution of KBr.
(g) Solid NaBr is treated with concentrated H_2SO_4.

(h) Chlorine is added to a solution of KI.

(i) Solid CaF_2 is treated with concentrated H_2SO_4.

(j) Solid MnO_2 is treated with concentrated hydriodic acid.

(k) A mixture of MnO_2 and $CaBr_2$ (solids) is treated with concentrated H_2SO_4.

(l) A solution of HF is allowed to stand in contact with glass.

(m) Bromine is dissolved in water.

(n) Iodine is added to a solution of KI in water.

(o) Solid KI is treated with concentrated H_2SO_4.

(p) Phosphorus tribromide (PBr_3) is added to water.

(q) A moistened paste of NH_4F is allowed to stand in contact with glass.

(r) A solution of Na_2CO_3 is treated with 0.1 *M* HBr.

(s) A solution of NH_4OH is treated with 0.1 *M* HCl.

(t) A solution of NaOH is treated with 0.1 *M* HF.

(u) A solution of 0.1 *M* HI is treated with magnesium.

(v) Hydrogen is burned in Cl_2 gas.

29. The following dual equilibrium exists in a solution of I_2 in 0.1 *N* KI.

$$HIO + H^+ + I^- \rightleftarrows H_2O + I_2; \qquad I_2 + I^- \rightleftarrows I_3^-$$

How will this dual equilibrium be affected by: (a) Addition of NaOH? (b) Addition of $Na_2S_2O_3$? (c) Addition of KI? (d) Addition of SO_3^{--}?

30. Ferric (Fe^{+++}) ions and Cl^- ions exist in solution in equilibrium with the complex $FeCl_4^-$ ion according to the equation

$$Fe^{+++} + 4\,Cl^- \rightleftarrows FeCl_4^-$$

How will the concentration of $FeCl_4^-$ ions be affected by: (a) addition of KCl? (b) addition of KOH?

31. Give the oxidation number of the element set boldface in each of the following: $\mathbf{Cl}^-$, $\mathbf{Br}_2$, **HI**, $\mathbf{Cu}^{++}$, $\mathbf{SO}_3^{--}$, $\mathbf{SO}_4^{--}$, $\mathbf{S}^{--}$, $H_2\mathbf{SO}_3$, $H_2\mathbf{S}$, $\mathbf{BiO}_3^-$, $\mathbf{Cr}_2(SO_4)_3$, $\mathbf{Cr}_2O_7^{--}$, $H_2\mathbf{O}_2$, $\mathbf{Sn}(OH)_4^{--}$, $K\mathbf{ClO}_3$, $\mathbf{Sb}_2O_5$, $Na_2\mathbf{SnO}_2$, $Na_2\mathbf{S}_2O_3$, $\mathbf{S}_4O_6^{--}$.

32. Balance the following equations.

(a) $Al + SnCl_4 = AlCl_3 + SnCl_2$

(b) $H_2SO_3 + HNO_3 = H_2SO_4 + H_2O + NO$

(c) $HgCl_2 + SnCl_2 = SnCl_4 + Hg_2Cl_2$

(d) $S + HNO_3 = H_2SO_4 + NO$

(e) $Bi(OH)_3 + Na_2SnO_2 = Bi + Na_2SnO_3 + H_2O$

(f) $FeCl_3 + H_2S = FeCl_2 + HCl + S$

(g) $As + HNO_3 + H_2O = H_3AsO_4 + NO$
(h) $C + H_2SO_4 = CO_2 + SO_2 + H_2O$
(i) $C + HNO_3 = CO_2 + NO + H_2O$
(j) $KClO_3 + Na_2SnO_2 = KCl + Na_2SnO_3$

33. Balance the following equations.
(a) $As_2S_3 + HNO_3 + H_2O = H_3AsO_4 + H_2SO_4 + NO$
(b) $Cu_2S + HNO_3 = Cu(NO_3)_2 + NO + S + H_2O$
(c) $KClO_3 = KCl + KClO_4$
(d) $FeS + H_2SO_4 = Fe_2(SO_4)_3 + SO_2 + H_2O$
(e) $Cu_2S + H_2SO_4 = CuSO_4 + SO_2 + H_2O$
(f) $HIO_3 + HI = H_2O + I_2$
(g) $Na_2SnO_2 + H_2O_2 = Na_2SnO_3 + H_2O$
(h) $Na_3CrO_3 + H_2O_2 = Na_2CrO_4 + NaOH + H_2O$
(i) $Na_2SnO_2 + Na_2O_2 + H_2O = Na_2SnO_3 + NaOH$
(j) $MnO_2 + H_2SO_4 + H_2C_2O_4 = CO_2 + MnSO_4 + H_2O$

34. Complete and balance the following equations.
(a) $Fe^{+++} + Sn^{++} = Fe^{++} + Sn^{++++}$
(b) $NO_3^- + S^{--} = NO + S$
(c) $ClO_3^- + SO_3^{--} = Cl^- + SO_4^{--}$
(d) $Sn + NO_3^- = SnO_2 + NO$
(e) $Zn + NO_3^- = Zn^{++} + NO_2$
(f) $I^- + NO_3^- = I_2 + NO$
(g) $MnO_4^- + SO_3^{--} = Mn^{++} + SO_4^{--}$
(h) $Cr_2O_7^{--} + SO_3^{--} = Cr^{+++} + SO_4^{--}$
(i) $Cr_2O_7^{--} + I^- = Cr^{+++} + I_2$
(j) $Fe^{++} + MnO_4^- = Fe^{+++} + Mn^{++}$

35. Complete and balance the following equations.
(a) $MnO_4^- + Br^- = Mn^{++} + Br_2$
(b) $MnO_4^- + Zn = Zn^{++} + Mn^{++}$
(c) $MnO_4^- + Sn^{++} = Mn^{++} + Sn^{++++}$
(d) $ClO_3^- + Fe^{++} = Cl^- + Fe^{+++}$
(e) $SnS + NO_3^- = SnO_2 + SO_4^{--} + NO_2$
(f) $SO_3^{--} + H_2O_2 = SO_4^{--} + H_2O$
(g) $MnO_4^- + Sn(OH)_4^{--} = MnO_2 + Sn(OH)_6^{--}$
(h) $Cr(OH)_4^- + Na_2O_2 = CrO_4^{--} + Na^+ + OH^-$

(i) $Bi(OH)_3 + Sn(OH)_4^{--} = Bi + Sn(OH)_6^{--}$

(j) $MnO_4^- + I^- = MnO_4^{--} + I_2$

36. Calculate the hydrolysis constant for 0.1 *M* NaF.

37. Calculate the concentration of F^- ions in a 0.01 *M* solution of NaF in 0.1 *M* $HC_2H_3O_2$.

38. Calculate the concentration in grams of solute per liter of solution of 0.1 *N* solutions of the substances set boldface when used in the indicated reactions.

(a) $2\,\mathbf{KMnO_4} + 3\,K_2SO_3 + H_2O = 2\,MnO_2 + 3\,K_2SO_4 + 2\,KOH$

(b) $ClO_3^- + 3\,\mathbf{H_2SO_3} = Cl^- + 6\,H^+ + 3\,SO_4^{--}$

(c) $6\,\mathbf{Fe}^{++} + Cr_2O_7^{--} + 14\,H^+ = 6\,Fe^{+++} + 2\,Cr^{+++} + 7\,H_2O$

39. It required 200 mg of $KClO_3$ to oxidize 49 ml of H_2SO_3 solution. Calculate the normality of the H_2SO_3.

40. How many grams of $FeSO_4$ will be oxidized to $Fe_2(SO_4)_3$ by 24 ml of 0.25 *N* $KMnO_4$ in a reaction in which the manganese is reduced to an oxidation number of +2?

41. How many milliliters of 0.5 *N* NaOH will be required to react with 0.2 gram-ion of Sn^{++} ion according to the reaction $Sn^{++} + 4\,OH^- = Sn(OH)_4^{--}$?

CHAPTER 17

Sulfur

Sulfuric acid is our most widely used synthetic chemical compound. It enters, directly or indirectly, into the manufacture of just about anything that you can name. Sulfur itself is required for vulcanization of the huge tonnages of rubber that are used in the manufacture of automobile and truck tires, for manufacture of many of the insecticides that are used to protect our crops, and for preparation of dyes and paints. More than 5,000,000 tons of sulfur are mined in the United States annually, and approximately 80% of this total is converted into sulfuric acid.

17.1 The properties of the group VIA elements (see Table 17.1). Although oxygen and sulfur are the only elements in group VIA that are considered in detail in this book, it is of interest to note the following relationships among the members of the group.

1. *Every member has 6 electrons in its valence shell.* That means that they are electronegative and tend to form divalent negative ions by accepting 2 electrons from electropositive elements. Oxygen is the most electronegative element in the group. (Among all the 100 elements only fluorine is more electronegative than oxygen.) They form covalent compounds by sharing 2 or more electrons with hydrogen or nonmetals to show oxidation numbers of -2, 4, and 6; the oxidation state of oxygen is -2, in rare instances -1. They illustrate the general rule, already noted in 16.11, which applies to all elements in groups IVA, VA, VIA, and VIIA, that the element tends to take its lowest (negative) oxidation state in its binary hydrogen compound and binary salts (compounds with metals), and its higher (positive) oxidation states in its oxides and ternary salts. Thus in the compounds H_2O, H_2S, H_2Se, H_2Te, MgO, Na_2S, CaSe, and BaTe, oxygen, sulfur, selenium, and tellurium all have oxidation states of -2, while in SO_2, SO_3, SeO_2, H_2SeO_3, TeO_2, and Na_2TeO_4 the oxidation states of S, Se, and Te are $+4$ or $+6$.

In binary compounds formed by the combination of two nonmetals, the more electronegative element has a negative oxidation number. Thus in S_2Cl_2 the oxidation number of sulfur is $+1$, while in P_4S_3 it is considered to be -4.

TABLE 17.1

THE GROUP VIA ELEMENTS

Element	Period	At. no.	At. wt	Atomic diam, Å	Electronic configuration	Density	Mp	Bp	Color and state	Electric conductivity	Common oxidation states
Oxygen	2	8	16.000	1.48	2, 6	1.429 (g/l)	−218.4°	−183°	colorless gas	nonconductor	−2, −1
Sulfur	3	16	32.066	2.08	2, 8, 6	2.07	119.0°	444.6°	yellow solid	nonconductor	−2, 4, 6
Selenium	4	34	78.96	2.34	2, 8, 18, 6	4.79	217.4°	688°	red solid	poor conductor	−2, 4, 6
Tellurium	5	52	127.61	2.74	2, 8, 18, 18, 6	6.25	452°	1390°	silver-white solid	fair conductor	−2, 4, 6
Polonium	6	84	(210)	3.06	2, 8, 18, 32, 18, 6				silver-gray solid	good conductor	

2. *Within the group as the atomic number increases:*

(a) The density increases.

(b) The melting point increases.

(c) The boiling point increases.

(d) The atomic diameter increases.

(e) The element becomes more metallic and less nonmetallic in its chemical and physical character.

(f) The electronegativity (reactivity) decreases.

(g) The oxidizing power of the element decreases. It is logical to

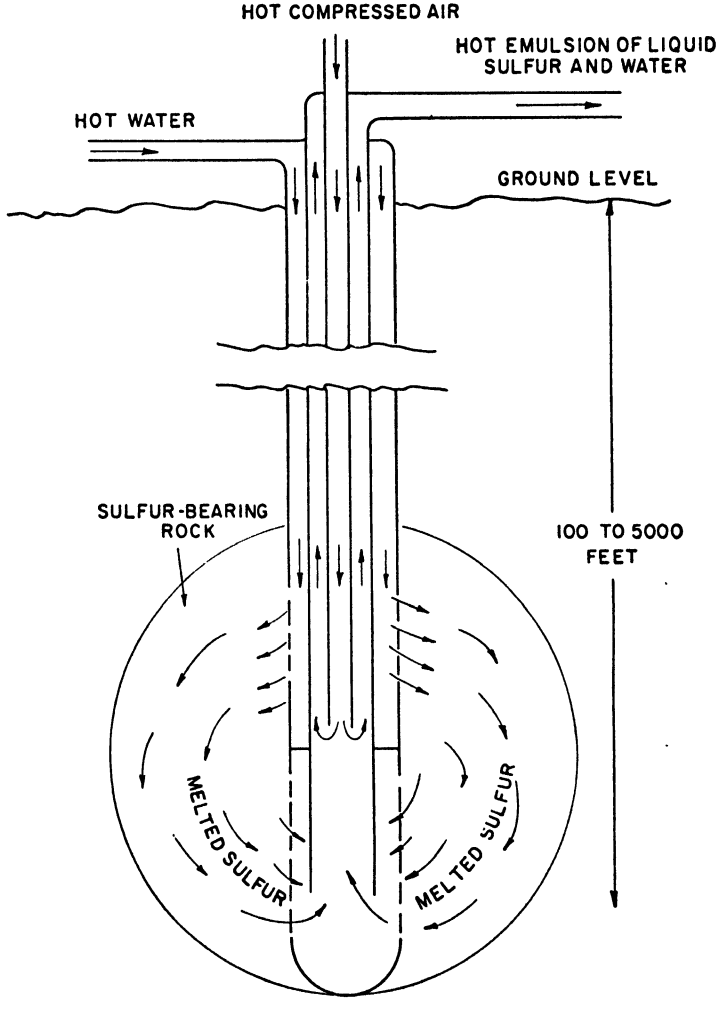


Figure 17.1. The Frasch process for the extraction of sulfur from underground deposits.

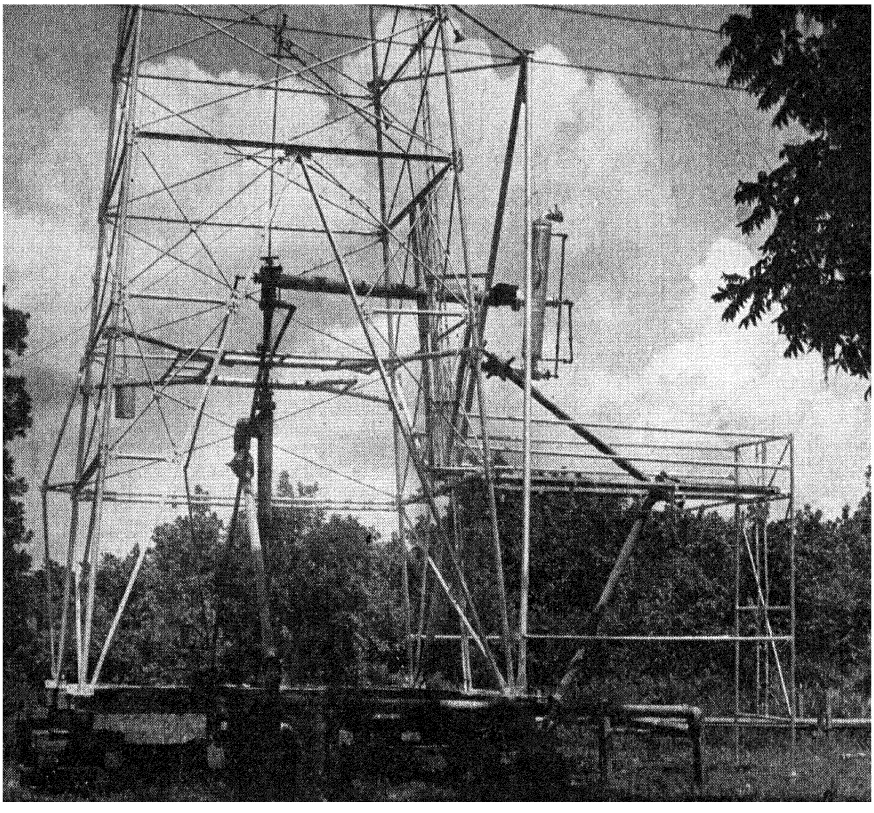


Figure 17.2. Surface piping equipment of a sulfur well. Hot water and compressed hot air, generated at a central power station, are piped to each well. The hot, melted sulfur, mixed with a small amount of water, is piped from the well to a central collecting station from which it flows to the solidification vats. (*Courtesy Texas Gulf Sulfur Company*)

postulate that decrease in electronegativity and oxidizing power result largely from the fact that the force with which electrons are attracted into the valence shell decreases as the distance from the nucleus to the shell increases. Although the charge on the nucleus increases as the atomic number increases, this is offset by the fact that the repulsion toward entering electrons by the electrons in the structure of the atom increases as the number of electrons in the structure increases (see 16.1).

(h) The electric conductivity increases. This is evidence of an increase in metallic character.

(i) The hydrogen compound becomes less stable toward heat. This is evidence of a decrease in nonmetallic character (increase in metallic character).

(j) The oxide becomes less acidic and more basic in character, and the binary and ternary acids become weaker.

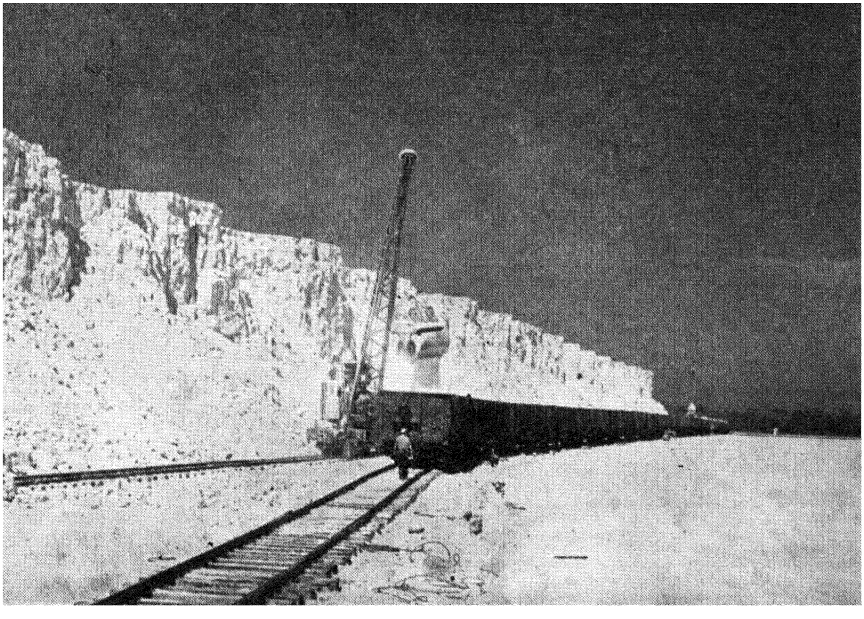
(k) The element is less plentiful in nature. Oxygen is the most plentiful of all elements, constituting 46.7% of the earth's crust. Sulfur

is present to the extent of less than 0.03%, while selenium, tellurium, and polonium are present in decreasing trace amounts.

3. The chemical similarity and similarity of oxidation state is evidenced by the compounds that are formed. Thus we find H_2O, H_2S, H_2Se, and H_2Te; CaO, CaS, CaSe, and CaTe; SO_2, SeO_2, and TeO_2; H_2SO_4, H_2SeO_4, and H_2TeO_4; SnO_2, SnS_2, $(NH_4)_2SnO_3$, $(NH_4)_2SnS_3$, C_2H_5OH, and C_2H_6SH.

4. The melting points of the binary hydrogen compounds are: H_2O, 0°; H_2S, −85.5°; H_2Se, −64°; H_2Te, −49°. The boiling points are: H_2O, 100°; H_2S, −60.3°; H_2Se, −41.3°; H_2Te, −2.2°. As previously noted, H_2S, H_2Se, and H_2Te follow the general rule that in a series of closely related compounds, the melting point and boiling point increase as the molecular weight increases. Water (H_2O) is out of line because its molecules are such strong dipoles; the molecules are firmly bound together by the electrostatic attraction of the dipoles and by hydrogen bonding. As a result, the melting point and boiling point are high. Attention has been called to the fact that the same property is shown by HF in comparison with HCl, HBr, and HI (see 16.2-2).

Figure 17.3. Man-made mountain of solid sulfur. These huge "vats" of 99.5% pure solid sulfur are formed by cooling the liquid that flows from the collecting station. A completed vat is about 1200 feet long, 250 to 300 feet wide and from 45 to 50 feet high and contains about 500,000 tons of sulfur. The solid sulfur in the vat is blasted loose with dynamite and loaded into flat cars with power shovels. At the far right a vat is in the process of being built up. *(Courtesy Texas Gulf Sulfur Company)*



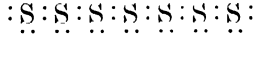
17.2 Occurrence of sulfur. It occurs as free sulfur (in commercial quantities, in the United States, Italy, and Sicily), as sulfides and sulfates of metals (ZnS, PbS, HgS, Ag_2S, Cu_2S, FeS_2, CdS, $CaSO_4 \cdot 2H_2O$, $BaSO_4$, Na_2SO_4, etc.), and to a limited extent as organic sulfur compounds. About 80% of the world's annual production of sulfur is mined in the United States by the Frasch process (see Figures 17.1, 17.2, and 17.3). About 76% of the annual United States production of approximately 5,000,000 tons comes from Texas, and 24% from Louisiana.

17.3 Physical properties of sulfur (see Table 17.1). The most distinctive physical property of sulfur is its existence, in the solid and liquid state, in different allotropic forms as represented by the following equilibria:

$$\text{S (rhombic)} \underset{}{\overset{96^\circ\text{C}}{\rightleftharpoons}} \text{S (monoclinic)} \overset{119^\circ\text{C}}{\rightleftharpoons}$$

$$\text{S (liquid } \lambda) \overset{200^\circ\text{C}}{\rightleftharpoons} \text{S (liquid } \mu) \overset{445^\circ\text{C}}{\rightleftharpoons} \text{S (vapor)}$$

Monoclinic sulfur melts at 119°C to form a fluid, light-straw-colored liquid; at about 200°C this liquid darkens in color, and very abruptly becomes extremely viscous. As the temperature increases from 200° to 400°, the viscosity gradually decreases until, at 400°C, a dark-amber-colored fluid liquid exists. If this liquid is chilled by pouring it into cold water a rubberlike plastic mass forms. This rubberlike form and the viscous modification noted at about 200° probably result from combination of sulfur atoms in the form of chainlike molecules.



It should be noted that rhombic sulfur crystals contain eight-member rings of sulfur atoms (S_8).

Monoclinic and rhombic sulfur are soluble in CS_2; viscous sulfur is insoluble.

17.4 Chemical properties of sulfur

1. Combines directly with metals to form sulfides (salts).

$$Zn + S = ZnS + \text{heat}$$

Note that in this reaction the sulfur acts as an oxidizing agent, while the metal is the reducing agent. The sulfides are electrovalent compounds; the metal transfers 2 electrons to the valence shell of the sulfur atom to form the S^{--} ion and the metal cation.

2. Combines directly with hydrogen to form H_2S.

$$H_2 + S \text{ (heated)} = H_2S$$

The H_2S is a covalent compound. The sulfur atom shares a pair of electrons with each of the two hydrogen atoms.

3. Burns in air or oxygen to form SO_2.

$$S + O_2 = SO_2 \text{ (gas)}$$

Oxygen is more strongly electronegative than S; therefore S functions as a reducing agent and is oxidized to an oxidation number of +4.

4. Combines directly with other nonmetals to form covalent compounds.

$$C + 2\,S = CS_2$$

5. Reacts with strong oxidizing agents such as concentrated H_2SO_4, concentrated HNO_3, $KClO_3$, KNO_3, Na_2O_2, etc. The product is SO_2, SO_3, or H_2SO_4, depending on the temperature and the concentration and oxidizing power of the oxidizing agent.

$$S + 2\,HNO_3 = H_2SO_4 + 2\,NO$$
$$S + 2\,H_2SO_4 = 3\,SO_2 + 2\,H_2O$$
$$S + KClO_3 = SO_3 + KCl$$

17.5 Some important commercial uses of sulfur. It is used for the manufacture of sulfuric acid (about 80% of total use), sulfur dioxide, sulfites, vulcanized rubber, insecticides such as lime-sulfur, dyes, paints, matches (see 19.8), and black gunpowder (a mixture of charcoal, sulfur, and potassium nitrate).

17.6 Laboratory preparation of H_2S. Sulfide of a metal + strong nonoxidizing acid = $H_2S\uparrow$ + a salt.

$$FeS + 2\,H^+ = Fe^{++} + H_2S\uparrow$$

The escape of the H_2S causes the reaction to be complete to the right. The evolved H_2S gas is colorless and has the foul odor of rotten eggs; it is very toxic and should never be inhaled in quantity. It can be identified by the fact that it gives a black precipitate with a solution of a lead salt.

$$Pb^{++} + H_2S = \mathbf{PbS} \text{ (black)} + 2\,H^+$$

17.7 Chemical properties of H_2S

1. Its water solution is a very weak acid (see 13.1).
2. It burns in air or oxygen.

$$2\,H_2S + 3\,O_2 = 2\,SO_2 + 2\,H_2O$$

If the flame is chilled below the kindling temperature of sulfur, or if the supply of air is limited, incomplete combustion takes place.

$$2\,H_2S + O_2 = 2\,H_2O + 2\,S$$

3. It is a fairly strong reducing agent. Since it contains sulfur in its lowest oxidation state, -2, it qualifies as a reducing agent, because the sulfur can be oxidized to states of 0, 4, or 6 (see 16.2–10).

$$3\,H_2S + 2\,NO_3^- \text{ (conc } HNO_3) + 2\,H^+ = 3\,S + 2\,NO + 4\,H_2O$$
$$H_2S + SO_4^{--} \text{ (conc } H_2SO_4) + 2\,H^+ = S + SO_2 + 2\,H_2O$$

These reactions show why nonoxidizing acids such as HCl or dilute H_2SO_4 must be used when preparing H_2S.

17.8 Uses of H_2S. It has no important commercial uses. It is an important reagent in qualitative analysis, where it is used to precipitate a number of the cations as insoluble sulfides.

$$Cd^{++} + H_2S = \mathbf{CdS} \text{ (yellow)} + 2\,H^+$$

17.9 Laboratory preparation of sulfur dioxide. It is prepared by the reaction of a sulfite or hydrogen sulfite of a metal with an acid.

$$Na_2SO_3 + 2\,H^+ = 2\,Na^+ + H_2O + SO_2\uparrow$$
$$NaHSO_3 + H^+ = Na^+ + H_2O + SO_2\uparrow$$

This is a typical salt + acid = new salt + new acid, type of reaction. The acid, H_2SO_3, is first formed, but being unstable, it immediately breaks down into H_2O and $SO_2\uparrow$. Because SO_2 escapes as a gas the reactions are complete.

The SO_2 gas that is evolved can be identified by its characteristic sharp, stifling odor and by the fact that it will decolorize iodine water and yield a solution containing sulfate ion; the sulfate ion can be identified by the fact that it gives a white precipitate, $BaSO_4$, with barium ions; this precipitate is insoluble in acids.

$$I_2 + H_2O \rightleftarrows H^+ + I^- + HIO$$
$$SO_2 + H_2O + HIO = SO_4^{--} + 3\,H^+ + I^-$$
$$SO_4^{--} + Ba^{++} = \mathbf{BaSO_4} \text{ (white, insoluble in acid)}$$

The SO_2 is quite soluble in water and is heavier than air; therefore it is collected by upward displacement of air.

17.10 Other sources of sulfur dioxide

1. Burning sulfur and sulfur compounds

$$S + O_2 = SO_2$$
$$2\,H_2S + 3\,O_2 = 2\,H_2O + 2\,SO_2$$

2. Roasting sulfide ores. *Roasting* involves heating a substance in the presence of air. An *ore* is a naturally occurring mineral which serves as the commercial source of an element or compound.

$$2\,ZnS + 3\,O_2 \text{ (heated)} = 2\,ZnO + 2\,SO_2$$
$$4\,FeS_2 + 11\,O_2 \text{ (heated)} = 2\,Fe_2O_3 + 8\,SO_2$$
$$HgS + O_2 \text{ (heated)} = Hg + SO_2$$

Noble metal sulfides yield the metal and SO_2 when roasted; base metal sulfides yield the metal oxide and SO_2.

3. Heating sulfites of all metals except those in group IA. The products are the metal oxide and SO_2.

$$CaSO_3 \text{ (heated)} = CaO + SO_2$$

This reaction illustrates the fact that if a ternary acid is unstable, its salts are, as a general rule, also unstable. The ternary salt decomposes to give a basic oxide and an acidic oxide. We will find that every ternary salt may be considered to be made up of an acidic oxide and a basic oxide. Thus $BaSO_4$ is $BaO + SO_3$, $CaCO_3$ is $CaO + CO_2$, $Cu(NO_3)_2$ is $CuO + N_2O_5$, and K_3PO_4 is $K_2O + P_2O_5$. The acidic oxide is in every instance the acid anhydride of the acid from which the salt is derived.

4. Heating the hydrogen sulfite of any metal

$$Ca(HSO_3)_2 \text{ (heated)} = CaO + H_2O + 2\,SO_2\uparrow$$
$$2\,NaHSO_3 \text{ (heated)} = Na_2SO_3 + H_2O + SO_2\uparrow$$

5. Reduction of concentrated H_2SO_4 by a moderately active reducing agent

$$2\,H_2SO_4 + Cu \text{ (heated)} = CuSO_4 + 2\,H_2O + SO_2\uparrow$$
$$2\,H_2SO_4 + S \text{ (heated)} = 3\,SO_2\uparrow + 2\,H_2O$$
$$H_2SO_4 + 2\,HBr = 2\,H_2O + SO_2\uparrow + Br_2\uparrow$$

The concentrated H_2SO_4 is the oxidizing agent; the oxidation number of the sulfur decreases from +6 in H_2SO_4 to +4 in SO_2. The Cu, S, and Br (in HBr) are oxidized.

17.11 Commercial sources of sulfur dioxide

1. Burning sulfur in air
2. Roasting sulfide ores (see 17.10–2)

17.12 Chemical properties of sulfur dioxide

1. It is the acid anhydride of sulfurous acid, H_2SO_3.

$$SO_2 + H_2O \rightleftarrows H_2SO_3 \rightleftarrows 2\,H^+ + SO_3^{--}$$

2. It is a moderately active reducing agent, being oxidized to SO_3.

$$2\,SO_2 + O_2 \rightleftarrows 2\,SO_3$$

This is the reaction that takes place in the *contact process* for making sulfuric acid. It can be carried out at 400–500°C in the presence of a catalyst (Pt, V_2O_5, Fe_2O_3, etc.).

$$SO_2 + NO_2 \rightleftarrows SO_3 + NO$$

This reaction occurs in the *lead chamber process* for making sulfuric acid.

3. In some instances it functions as an oxidizing agent. Since it contains sulfur in one of its higher oxidation states, it is qualified to act as an oxidizing agent in the presence of a strong enough reducing agent.

$$SO_2 + 4\,HI\ (\text{heated}) = S + 2\,H_2O + 2\,I_2$$

17.13 Commercial uses of SO_2. Its important uses include manufacture of H_2SO_4 and sulfites, bleaching textiles and straw, preservation of dried fruits, and as a refrigerant. The last use depends upon the fact that SO_2 gas is easily liquefied and has a very high heat of vaporization (see 2.17).

17.14 Properties of sulfurous acid

1. It is unstable toward heat. As a result its solution has the characteristic odor of SO_2.

$$H_2SO_3 \rightleftarrows H_2O + SO_2\uparrow$$

2. It is a weak acid. It is stronger, however, than acetic acid. It shows the characteristic properties of acids as discussed in Section 13.1, page 253.

3. It is a fairly strong reducing agent. In this reaction the sulfur is oxidized to its highest state, +6.

$$ClO_3^- + 3\,H_2SO_3 = 3\,SO_4^{--} + Cl^- + 6\,H^+$$

$$Cr_2O_7^{--} + 3\,H_2SO_3 + 2\,H^+ = 2\,Cr^{+++} + 3\,SO_4^{--} + 4\,H_2O$$

The formation of a white precipitate of $BaSO_4$ on treatment with Ba^{++} is proof that oxidation to SO_4^{--} has occurred.

The reducing property of the H_2SO_3 that is formed when SO_2 comes in contact with moisture is the basis for the use of SO_2 as a bleaching agent and dried fruit preservative. The identification of SO_2 by its ability to decolorize iodine solution is dependent upon the reducing property of H_2SO_3.

17.15 Properties of sulfur trioxide

1. It is the acid anhydride of H_2SO_4.

$$SO_3 + H_2O = 2\,H^+ + SO_4^{--}$$

2. It is a colorless liquid which fumes strongly in moist air and boils at 44.6°C. In the presence of small amounts of moisture it solidifies to white crystals of hydrated SO_3.

17.16 Commercial preparation of sulfuric acid

1. Catalytic oxidation of SO_2 to SO_3 by O_2 in the contact process (see 17.12 and Figure 17.4). Over 70% of the United States production is by this method. The catalysts (V_2O_5 or platinum) are easily poisoned, so the SO_2 gas must be carefully purified. The SO_2 that is used is prepared either by burning S or by roasting sulfide ores. In the latter case the

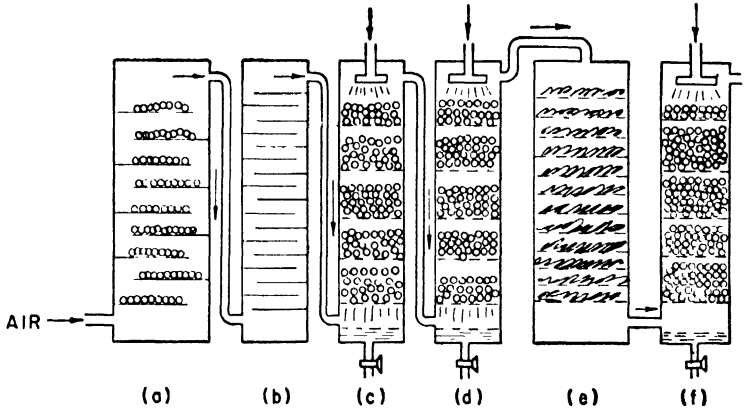


Figure 17.4. Contact process for the manufacture of sulfuric acid. (a) Sulfur burner. SO_2 is formed by burning sulfur or roasting a sulfide. (b) Dust settling tower. (c) Water scrubbing tower for removing water-soluble impurities. (d) Drying tower: moisture removed by washing with concentrated sulfuric acid. (e) Catalytic reaction tower. (f) Absorption tower: the SO_3 gas is absorbed in concentrated sulfuric acid. 98% sulfuric acid is drawn off from the bottom of this tower.

manufacture of H_2SO_4 is carried out in conjunction with the metallurgy of metals. The sulfur dioxide gas from the roasting of ores becomes a nuisance if allowed to escape into the air; by converting it into H_2SO_4 the nuisance is avoided and a valuable by-product is produced.

The platinum or V_2O_5 functions as a catalyst by adsorbing the SO_2 and O_2 on its surface, thereby promoting their interaction. The SO_3 is

not so strongly adsorbed, and therefore escapes to make room for adsorption of more SO_2 and O_2.

The SO_3 that is formed is absorbed in moderately concentrated H_2SO_4. Pure water or steam will not wet SO_3 but the concentrated acid will.

The contact process yields 98% acid of very high purity. It is a colorless "oily" looking liquid which boils at about 338°C and has a density of about 1.84 g/cc.

2. Oxidation of SO_2 to SO_3 by NO_2 in the lead chamber process. The reaction is carried out in lead-lined reaction chambers of large volume. A mixture of steam, SO_2, and NO_2 is introduced; the reaction that takes place is fairly complex, a compound known as nitrosyl sulfuric acid and having the formula $NO_2 \cdot SO_2OH$ being formed as an intermediate. The over-all reaction can, however, be represented by the equations

$$NO_2 + SO_2 = NO + SO_3$$
$$SO_3 + H_2O = 2\,H^+ + SO_4^{--}$$

The lead chamber process has the advantage that the SO_2 gas need not be particularly pure, since there is no catalyst to be poisoned. The acid that is produced is relatively dilute and of lower purity than contact acid. As already noted, only about 30% of our annual production of H_2SO_4 is made by the chamber process.

17.17 Chemical properties of sulfuric acid

1. Its solution is a strong acid and shows all the properties listed in Section 13.1 on page 253.

2. Concentrated sulfuric acid is an oxidizing agent. It qualifies as an oxidizing agent because it contains, in an oxidation state of 6, the element sulfur, which also has oxidation numbers of 4, 0, and −2. Moderate reducing agents reduce it to H_2SO_3 or SO_2; very strong ones will reduce it to H_2S and S.

$$H_2SO_4 + 2\,HBr\ (gas) = 2\,H_2O + SO_2 + Br_2$$
$$H_2SO_4 + 6\,HI = 4\,H_2O + S + 3\,I_2$$
$$H_2SO_4 + 8\,HI = 4\,H_2O + H_2S\uparrow + 4\,I_2$$
$$Zn + 2\,H_2SO_4\ (conc) = Zn^{++} + SO_4^{--} + SO_2\uparrow + 2\,H_2O$$

3. Concentrated sulfuric acid is a powerful dehydrating agent. It has such a strong affinity for water, with which it combines to form a hydrate, that not only will it remove free moisture from the air, but it will also extract the components of water from carbohydrates and similar organic compounds containing oxygen and hydrogen.

$$(C_6H_{10}O_5)_x \text{ (cellulose)} + X\ H_2SO_4 \text{ (conc)} = X\ H_2SO_4 \cdot 5H_2O + 6\ C$$
$$C_{12}H_{22}O_{11} \text{ (sugar)} + X\ H_2SO_4 \text{ (conc)} = X\ H_2SO_4 \cdot 11H_2O + 12\ C$$

The combination of H_2SO_4 with H_2O is a highly exothermic reaction. As a result, a large amount of heat is evolved when concentrated sulfuric acid is added to water or a carbohydrate. Because of its combined dehydrating and oxidizing powers, hot concentrated H_2SO_4 produces severe burns when it comes in contact with the skin.

17.18 Some important commercial uses of sulfuric acid. Of the approximately 10,000,000 tons of 98% sulfuric acid that are produced annually in the United States at the present time, about 31% is used in the manufacture of fertilizers, 25% in the manufacture of chemicals, both organic and inorganic, and 12% in the manufacture of gasoline, lubricating oil, and other petroleum products. The manufacture of iron, steel, coal tar derivatives, paints, pigments, rayon, and plastics together consume about 24%, while the manufacture of explosives, nonferrous metals, and textiles uses about 5.5%. The remaining 2.5% includes a variety of uses, the most important of which is as the electrolyte in lead storage batteries for use in automobiles and trucks.

The two most important fertilizers that use H_2SO_4 in their preparation are ammonium sulfate, $(NH_4)_2SO_4$, and superphosphate, $Ca(H_2PO_4)_2 + 2\ CaSO_4$. The former is obtained by combining NH_3 with H_2SO_4,

$$2\ NH_3 + H_2SO_4 = (NH_4)_2SO_4$$

while the latter is formed when natural rock phosphate $Ca_3(PO_4)_2$ is treated with concentrated H_2SO_4.

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 = Ca(H_2PO_4)_2 + 2\ CaSO_4$$

In the iron, steel, and nonferrous metal industries, the acid functions largely as a *pickling* agent to remove the oxide scale.

$$Fe_2O_3 + 6\ H^+ = 2\ Fe^{+++} + 3\ H_2O$$
$$CuO + 2\ H^+ = Cu^{++} + H_2O$$

The other uses of H_2SO_4 are dependent in most cases upon its character as a strong, nonvolatile acid; its oxidizing and dehydrating properties may, in some instances, be involved.

Questions and Problems

1. Give the simple electronic configuration (electrons in each shell) of each of the elements in group VIA.

2. Arrange the group VIA elements in the order of their increasing: (a) atomic numbers; (b) atomic weights; (c) melting points; (d) boiling points; (e) densities; (f) atomic diameters; (g) electronegativity; (h) electropositivity; (i) nonmetallic character; (j) metallic character; (k) oxidizing strength.

3. Arrange the binary hydrogen compounds of the group VIA elements in the order of their increasing: (a) freezing points; (b) boiling points; (c) stability; (d) strength as reducing agents.

4. Arrange the oxides of the group VIA elements in the order of: (a) decreasing acidic character; (b) increasing basic character.

5. Arrange the ternary acids of the group VIA elements in the order of their decreasing strength.

6. Arrange the following in the order of increasing *p*H. (a) 0.1 *N* H_2S, 0.1 *N* H_2SO_3, 0.1 *N* H_2SO_4, 0.1 *N* K_2SO_4; (b) 1 *M* Na_2S, 1 *M* Na_2SO_3, 1 *M* Na_2SO_4, 1 *M* $CuSO_4$.

7. How could you demonstrate that sulfur is a nonmetal? Give net equations for all reactions that take place.

8. How do you account for the fact that S is less electronegative than O and Cl, but more electronegative than Se, Te, and P?

9. The compounds H_2S, SO_2, and SO_3 are covalent. Sketch each of these molecules, showing the arrangement of electrons and the character of the valence bonds. Sketch also the covalent molecules H_2SO_3 and H_2SO_4.

10. What is the oxidation number of S in each of the following? S, S^{--}, SO_3^{--}, SO_4^{--}, H_2S, SO_2, SO_3, H_2SO_3, H_2SO_4, $Na_2S_2O_3$, $Na_2S_4O_6$, $S_2O_3^{--}$, $S_4O_6^{--}$? Which of these substances can function as oxidizing agents? Which can function as reducing agents?

11. How could you demonstrate, by all available methods, that dilute H_2SO_4 is an acid?

12. How could you demonstrate, by all available methods, that H_2SO_4 is a stronger acid than H_2SO_3?

13. How do you account for the fact that a water solution of K_2SO_3 reacts alkaline to litmus, while K_2SO_4 is neutral and $(NH_4)_2SO_4$ is acidic? Give detailed equations for all reactions involved.

14. How could you demonstrate that H_2SO_3 and H_2S are reducing agents? Give net equations for all reactions involved.

15. How could you demonstrate that concentrated H_2SO_4 is an

oxidizing agent? That it is a dehydrating agent? Give net equations for reactions involved.

16. How can you distinguish between solutions of the following: HCl, HBr, HI, H_2S, H_2SO_3, H_2SO_4? Give net equations for all reactions.

17. How can you distinguish between the following solids: NaCl, NaI, Na_2S, Na_2SO_3, Na_2SO_4, Na_2CO_3, NaBr? Give net equations for all reactions.

18. Give net equations for four methods for preparing $MgSO_4$.

19. Given elementary sulfur as the source of S, and any other materials that you need, write equations to show how you could prepare: SO_2; SO_3; H_2SO_3; H_2SO_4; H_2S; ZnS; $ZnSO_4$.

20. List three chemical properties of H_2SO_4 and illustrate each with appropriate equations.

21. Write net equations for the identification of each of the following ions: Cl^-; I^-; S^{--}; SO_3^{--}; SO_4^{--}.

22. How would you prove that egg yolk contains sulfur?

23. Describe, with all equations and a sketch of the apparatus, how SO_2 gas is prepared and collected in the laboratory.

24. Outline in detail how SO_2 and H_2SO_4 are prepared, commercially, from (a) sulfur; (b) a sulfide ore. Give equations for all reactions.

25. Write net equations to illustrate:
   (a) Two chemical properties of SO_2.
   (b) Two chemical properties of a solution of H_2SO_3.
   (c) Two chemical properties of H_2S.
   (d) Three chemical properties of S.
   (e) Hydrolysis of Na_2S.
   (f) Formation in the laboratory of a solution of sulfuric acid.
   (g) Roasting of a sulfide ore.
   (h) Complete combustion of H_2S gas.

26. Write net equations for the reactions that take place when:
   (a) Sulfur dioxide gas is passed into a solution of bromine in water.
   (b) Hydrogen sulfide gas is passed into a solution of iodine in water.
   (c) Concentrated H_2SO_4 is added to dry NaCl.
   (d) A solution of H_2SO_4 is treated with a solution of KOH.
   (e) A solution of H_2S is treated with 1 *M* NH_4OH.
   (f) Hydrogen sulfide gas is passed into a solution of $Pb(NO_3)_2$.

(g) The presence of SO_4^{--} ions in a solution is proved.
(h) Hydrochloric acid is added to 1 M Na_2S.
(i) Hydrogen gas is passed over heated CuS.

27. Complete and balance the following equations.

$MnO_4^- + H_2SO_3 = Mn^{++} + SO_4^{--}$
$Cr_2O_7^{--} + H_2S = Cr^{+++} + S$
$I_2 + H_2S = S + I^-$
$Fe^{+++} + H_2S = Fe^{++} + S$
$S + NO_3^- = SO_4^{--} + NO$
$H_2SO_4 + S = SO_2 + H_2O$

28. Calculate the hydrolysis constant for 0.1 M K_2S.

29. How many liters of O_2 gas will be required for complete combustion of 60 l of H_2S gas? All measurements are made at the same temperature and pressure.

30. How many cubic centimeters of 98% H_2SO_4 whose density is 1.84 g/cc will be required for the preparation of 2 l of 0.4 N H_2SO_4?

31. What is the normality of 0.005 M H_2SO_4?

32. In 3.6 M H_2SO_4 there is 29% H_2SO_4. Calculate the density of 3.6 M H_2SO_4.

33. To what volume must 44.2 cc of 70.0% sulfuric acid whose density is 1.61 g/cc be diluted to give 0.800 N H_2SO_4?

34. It required 100 cc of a 12% solution of KOH of density 1.15 to neutralize 800 ml of sulfuric acid. Calculate the normality of the acid.

35. How many milliliters of 0.2 N Na_2SO_3 will be required to reduce 200 ml of 0.01 N $KMnO_4$?

36. Give the detailed electronic configuration (s, p, d, and f electrons) of each of the group VIA elements.

CHAPTER 18

Nitrogen

18.1 The group VA elements (see Table 18.1). The group VA elements illustrate, more strikingly than those of any other group, the decrease in nonmetallic character and increase in metallic character as the atomic number increases in a group. Nitrogen and phosphorus are typical nonmetals, while bismuth is definitely metallic; arsenic is distinctly nonmetallic but shows some characteristics of a metal. Antimony, on the other hand, is distinctly metallic but shows some of the characteristics of a nonmetal. The transition from nonmetal to metal in going from nitrogen to bismuth is evidenced in the following ways.

1. Nitrogen and phosphorus are nonconductors of electricity, arsenic is a poor conductor, antimony is good, and bismuth is excellent.

2. Nitrogen is a gas, phosphorus is a soft, waxy, lusterless solid; arsenic is a hard, lusterless solid; antimony and bismuth have the characteristic luster of typical metals.

3. There is a pronounced increase in hardness and density of the solid element in going from phosphorus to arsenic to antimony to bismuth.

4. The binary hydrogen compounds decrease in stability toward heat. Ammonia (NH_3) is very stable, while phosphine (PH_3), arsine (AsH_3), stibine (SbH_3), and bismuthine (BiH_3) are increasingly unstable. In the hydrogen compounds the elements have their lowest oxidation number, -3.

5. The oxides decrease in acidity and solubility in water. The oxides N_2O_3, N_2O_5, P_2O_3, P_2O_5, As_2O_3, and As_2O_5 are typical acid anhydrides and dissolve in water to form ternary acids; Sb_2O_3 and Sb_2O_5 are insoluble and weakly acidic; Bi_2O_3 is a typical insoluble basic oxide of a metal. In their oxides, and the ternary acids and salts derived from them, the elements have their higher oxidation numbers of $+3$ and $+5$.

6. The ternary acids decrease in strength and solubility in water. Nitric acid is strong, H_3PO_4 is weak, H_3AsO_4 is weaker, and H_3SbO_3 is so weak that it is amphoteric in character. The compound $H_3BiO_3[Bi(OH)_3]$ is a typical basic hydroxide of a metal. Nitric acid, H_3PO_4, and H_3AsO_4 are soluble, while H_3SbO_3 and $Bi(OH)_3$ are insoluble.

TABLE 18.1

THE GROUP VA ELEMENTS

Element	Period	At. no.	At. wt	At. diam, Å	Configuration	Density	Mp	Bp	Color and state	Electric conductivity	Stable oxidation states
Nitrogen	2	7	14.008	1.48	2, 5	1.25 g/l	−209.9°	−195.8°	colorless gas	nonconductor	−3, −2, −1, 1, 2, 3, 4, 5
Phosphorus	3	15	30.98	2.20	2, 8, 5	1.82 g/cc	44.1°	280°	pale yellow solid	nonconductor	−3, 3, 4, 5
Arsenic	4	33	74.91	2.42	2, 8, 18, 5	5.73	615°	814°	gray solid	poor conductor	−3, 3, 5
Antimony	5	51	121.76	2.82	2, 8, 18, 18, 5	6.68	630°	1380°	silvery white solid	good conductor	−3, 3, 5
Bismuth	6	83	209.00	3.04	2, 8, 18, 32, 18, 5	9.80	271°	1470°	bluish white solid	excellent conductor	3, (4)

7. The chlorides of nitrogen, phosphorus, and arsenic hydrolyze to yield two acids, the chloride of antimony yields a basic salt and an acid, while bismuth chloride yields Bi^{+++} and Cl^- ions, which hydrolyze to form the weak base $Bi(OH)_3$ and the ions of the strong acid HCl.

8. The number of stable oxidation states in which the element can exist decreases as the atomic number increases. Nitrogen has 8 stable states ranging from -3 to $+5$, while bismuth has only one common state, $+3$. In the presence of very strong oxidizing agents bismuth can exist in the $+4$ and $+5$ states. As a general rule the oxidation state of an element is determined by the conditions under which it exists. It is characteristic of nonmetals that they have a number of covalent oxidation states; in contrast, metals lose electrons to form ions, and therefore generally have few oxidation states. The decrease in the number of oxidation states and the decrease in the stability of the binary hydrogen compound with increase in atomic number of the element in a group are probably the result of a number of factors; prominent among these factors is the concept that as the diameter of the atom increases, the force with which foreign electrons are pulled into the valence shell decreases; this is because (1) the valence shell is farther away from the positive nucleus, and (2) there are more shielding electrons to repel the foreign electrons. These two effects more than offset the increase in attraction that results from the increase in the charge on the nucleus (the atomic number).

Because antimony and bismuth behave like metals they will be discussed along with the other metals in later chapters. Since arsenic is more like antimony than nitrogen and phosphorus it will be discussed along with antimony and bismuth in Chapter 28. Phosphorus will be considered in Chapter 19.

18.2 The importance of nitrogen. Nitrogen is one of the uniquely important elements. As a relatively inactive and inert component of the air it acts as a diluent for the oxygen and thereby helps to maintain oxidation processes at a normal desirable rate. It is a constituent of all proteins, and these proteins are absolutely essential for development of plant and animal tissue. Thus we find plants needing nitrogen fertilizer if they are to grow and store up nitrogen-containing protein. Animals, including man, must eat this plant protein, or the protein of other animals, if they are to build up their own protein-containing tissues. All the major explosives except the components of thermonuclear weapons (A bombs and H bombs) are nitrogen compounds.

18.3 Occurrence of nitrogen

1. As free nitrogen gas it constitutes about 79% of the volume of air.

2. It is a constituent of plant and animal protein. About 3% of the weight of the human body is nitrogen.

3. It occurs as Chile saltpeter ($NaNO_3$).

18.4 Laboratory preparation of nitrogen, by treating the nitrite of a metal with an ammonium salt

$$NO_2^- + NH_4^+ = 2\,H_2O + N_2\uparrow$$

Since nitrogen is insoluble in water it can be collected by displacement of water. Because it is a colorless, odorless, tasteless, inactive gas it is identified, negatively, by the fact that it will extinguish a burning splint.

18.5 Commercial preparation of nitrogen

1. From air, by removing the oxygen as CO_2

$$C\ (coke) + air = CO_2 + nitrogen$$

The CO_2 is washed out with water ($CO_2 + H_2O = H_2CO_3$); this leaves nitrogen mixed with the small per cent of argon, helium, neon, and xenon originally present in the air.

2. By fractional distillation of liquid air (see 3.23 A)

18.6 Chemical properties of nitrogen. Nitrogen is very inactive. The relatively few reactions which it does undergo are, however, very important because they represent the first step in the "fixation" of atmospheric nitrogen. As has already been noted, plants require nitrogen in order to build up the protein in their tissue, seeds, and fruit. They are, however, unable to assimilate the elemental nitrogen from the atmosphere; they can use it only when it exists in the form of compounds. Because most soils contain insufficient nitrogen compounds to support normal agricultural crop requirements, these compounds must be added as fertilizers. Nitrogen to supply the needs of agriculture and industry is obtained by *fixation of atmospheric nitrogen*, that is, by converting free nitrogen into nitrogen compounds. The important fixation processes are:

1. *Natural fixation by leguminous plants*, such as alfalfa, clover, beans, and peas. Nitrifying bacteria which are harbored in nodules on the roots of these plants convert the atmospheric nitrogen which diffuses into the soil into nitrites and nitrates (see Figure 18.1). The legume itself, as well as nonleguminous plants, can utilize these nitrites and nitrates and convert them into plant protein. Enormous tonnages of nitrogen are fixed each year by the large acreages of alfalfa, soy beans, and clover that are grown all over the world.

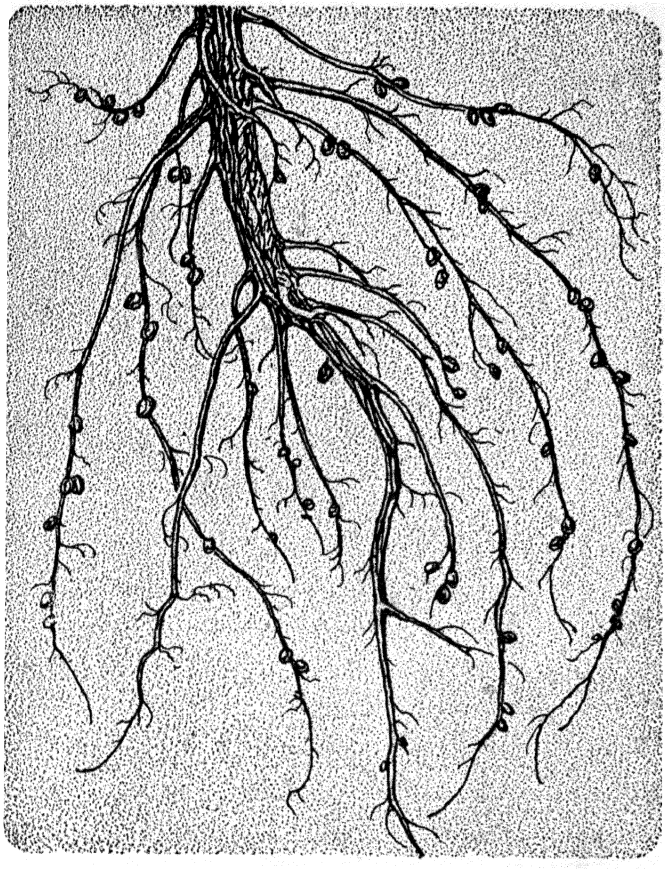


Figure 18.1. Nodules containing nitrifying bacteria on roots of soybean plant (greatly enlarged).

In addition to the nitrifying bacteria noted above, there are also denitrifying bacteria which act upon nitrogen compounds and convert them back to nitrogen. As a result of the combined activity of both kinds of bacteria and the various commercial processes whereby nitrogen is consumed and evolved, a *cycle* is set up whereby the nitrogen content of the air remains practically constant. This *nitrogen cycle* may be represented as in Figure 18.2.

2. *Commercial fixation* by

(a) *The Haber process*

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

The reaction is carried out at 400–500°C, at pressures of 150 to 2000 atm, and in the presence of iron as a catalyst. Practically all fixed

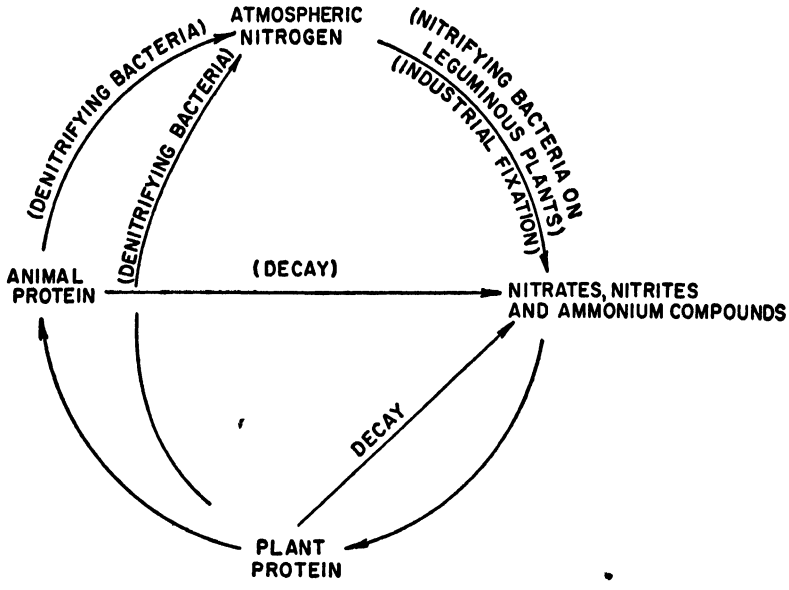


Figure 18.2. The nitrogen cycle.

nitrogen in the United States is obtained by this process. The high pressure speeds up the rate of the reaction by increasing the concentration of the reactants; it also shifts the equilibrium point to the right, because the total volume of the reactant gases is twice that of the products. The process yields pure anhydrous ammonia.

(b) *The arc process.* A high-voltage electric arc is passed through air. At the temperature of 2000–2500°C which is attained, from 1 to 2% of the nitrogen in the air is converted to NO. This NO then reacts slowly with more oxygen to form NO_2. This NO_2 can then be dissolved in water to give dilute HNO_3.

$$N_2 + O_2 \rightleftarrows 2\,NO$$
$$2\,NO + O_2 = 2\,NO_2$$
$$3\,NO_2 + H_2O = 2\,HNO_3 + NO$$

The original arc process is too expensive to compete with the more efficient Haber process. A modification of the arc process in which the source of heat is combustion of natural gas shows promise of becoming commercially practical.

(c) *The cyanamide process*

$$CaC_2 \text{ (calcium carbide)} + N_2 \xrightarrow{1200°C} C + CaCN_2 \text{ (calcium cyanamide)}$$

18.7 Laboratory preparation of ammonia

Ammonium salt + a strong base = new salt + NH_3 + H_2O

$$2\,NH_4Cl + CaO + (H_2O) = CaCl_2 + 2\,NH_3 + 2\,H_2O$$

A mixture of NH_4Cl and CaO is moistened to a paste and is then warmed. The colorless gas NH_3 is very soluble in water and is lighter than air. Therefore it is collected by downward displacement of air. It can be identified in the following ways:

1. It has a characteristic odor.

2. It turns moist red litmus paper blue. This is because it dissolves in water to form the weak base whose formula is generally represented as NH_4OH.

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

3. It yields a heavy white cloud of NH_4Cl when brought in contact with HCl gas or concentrated hydrochloric acid.

$$NH_3 + HCl = NH_4Cl \text{ (white)}$$

18.8 Commercial preparation of ammonia

1. From atmospheric nitrogen by the Haber process (see 18.6). This is the chief industrial source.

2. Destructive distillation of soft coal. Coal is formed as a result of the carbonization, during prehistoric times, of vegetable material at high temperatures and pressures. Since vegetable material contains proteins, the coal that is produced from it contains uncarbonized proteins and other nitrogen compounds. When this coal is heated to high temperatures (up to 1200°C) in the absence of air, the nitrogen which it contains is liberated largely in the form of NH_3 gas. The process of heating complex organic substances (wood, coal) in the absence of air to temperatures at which their component compounds are broken down is called *destructive distillation.* Other products of the destructive distillation of coal are coke, coal tar, carbon monoxide, carbon dioxide, and steam.

3. By the reaction of calcium cyanamide with steam

$$CaCN_2 + 3\,H_2O = CaCO_3 + 2\,NH_3$$

The annual production of ammonia in the United States is about 2,000,000 tons; approximately 90% is prepared by the Haber process.

18.9 Chemical properties of ammonia

1. It yields the weak base NH_4OH when dissolved in water.

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

2. It reacts with acids to form salts. This illustrates its property as a basic anhydride.

$$NH_3 + H^+ + Cl^- = NH_4^+ + Cl^-$$
$$2\,NH_3 + 2\,H^+ + SO_4^{--} = 2\,NH_4^+ + SO_4^{--}$$
$$NH_3 + H^+ + NO_3^- = NH_4^+ + NO_3^-$$

The latter two reactions represent commercial preparation of ammonium sulfate and ammonium nitrate fertilizers by absorption of NH_3 gas in sulfuric and nitric acids.

3. It is decomposed by heat.

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

At about 800°C and 760 mm the decomposition is about 98% complete and proceeds at a rapid rate. This is the basis for the use of liquid ammonia by the weather bureau and armed forces as a source of hydrogen for filling small test balloons.

4. It will reduce the less stable metal oxides.

$$3\,CuO + 2\,NH_3\ (\text{heated}) = 3\,Cu + 3\,H_2O + N_2\uparrow$$

What happens, probably, is that the NH_3 is first decomposed into N_2 and H_2, and the H_2 then reduces the CuO.

5. It can be oxidized by oxygen in the presence of a catalyst to give NO. This is the first step in the *Ostwald process* for preparation of nitric acid from ammonia.

$$4\,NH_3 + 5\,O_2 = 4\,NO + 6\,H_2O$$

The process is carried out at 400–900°C and 1 to 8 atm in the presence of platinum as a catalyst. The NO that is formed reacts with more oxygen to form NO_2.

$$2\,NO + O_2 = 2\,NO_2$$

This NO_2 is dissolved in water to yield HNO_3.

$$3\,NO_2 + H_2O = 2\,HNO_3 + NO$$

18.10 Commercial uses of ammonia. The most important uses are: manufacture of ammonium sulfate (for fertilizers), ammonium nitrate (for fertilizers), nitric acid, ammonium chloride (for dry batteries), and urea (for fertilizers). Direct application to the soil as a fertilizer in the form of pure, anhydrous ammonia; this process although relatively new, is rapidly growing in popularity, and on larger farms is replacing the use of ammonium compounds. As a refrigerant; this use

depends upon the fact that it is readily liquefied (critical temperature of 137.4° and boiling point of −33.3°) and has an extremely high heat of vaporization (310 cal/g at −10°C). The 1950 production of ammonium sulfate in the United States was about 2,000,000 tons, and of ammonium nitrate about 1,300,000 tons.

18.11 Laboratory preparation of nitric acid. Nitric acid may be prepared by treating the nitrate of a metal with concentrated sulfuric acid

$$NaNO_3 + H_2SO_4 \text{ (conc., heated)} = NaHSO_4 + HNO_3 \uparrow$$

This is a typical, salt + nonvolatile acid = new salt + new acid, reaction. Because of the corrosive action of HNO_3 on cork and rubber, the reaction must be carried out in an all-glass retort (see Figure 18.3). The HNO_3 that distills over boils at 86°C and has a density of 1.5. It generally has a brown color due to the presence of dissolved NO_2 gas formed by thermal decomposition of some of the HNO_3.

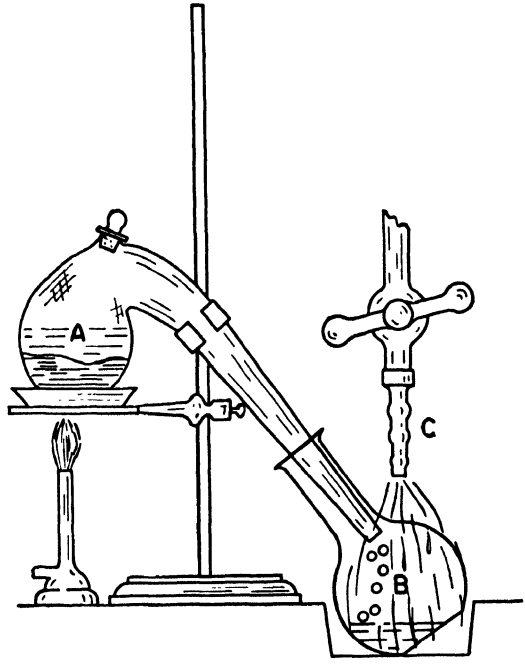


Figure 18.3. Laboratory preparation of nitric acid. A mixture of solid $NaNO_3$ and concentrated H_2SO_4 is heated in the all-glass retort, *A*. The HNO_3 that distills over is condensed in flask *B* by the stream of cold water from the tap *C*.

$$4\,HNO_3\ (\text{heated}) = 2\,H_2O + O_2 + 4\,NO_2\ (\text{brown gas})$$

18.12 Commercial preparation of nitric acid

1. Oxidation of ammonia by the Ostwald process (see 18.9–5). This is the chief commercial source.

2. From Chile saltpeter ($NaNO_3$)

$$NaNO_3 + H_2SO_4\ (\text{conc., heated}) = NaHSO_4 + HNO_3\uparrow$$

The annual production of nitric acid in the United States is about 500,000 tons. About 80% is prepared by the Ostwald process.

18.13 Chemical properties of nitric acid

1. It is a strong acid and shows all the properties given in Section 13.1, page 253.

2. It is a powerful oxidizing agent. It qualifies for this property because it contains in a higher oxidation state an element (N) which can exist in several lower states. When it reacts as an oxidizing agent, it is generally reduced either to NO or NO_2. Reduction to NO usually takes place when the HNO_3 is moderately concentrated, the temperature is not too high, and the reducing agent is very active. Reduction to NO_2 is favored when the acid is very concentrated, the temperature is high, and the reducing agent is less active. The liberation of brown fumes of NO_2 with a reducing agent is an excellent identification test for nitric acid. Nitric acid will oxidize the following classes of reducing agents:

(a) *All metals except* Au, Pt, *and* Ir. The products will be the oxide of nitrogen (either NO or NO_2 depending upon the conditions as noted above), H_2O, and metal nitrate. Polyvalent metals (Fe, Sn, Hg) will take their higher oxidation states.

$$Cu + 2\,NO_3^- + 4\,H^+ = Cu^{++} + 2\,NO_2\uparrow + 2\,H_2O$$
$$3\,Zn + 2\,NO_3^- + 8\,H^+ = 3\,Zn^{++} + 2\,NO\uparrow + 4\,H_2O$$

This serves as a means of preparing NO and NO_2. It should be noted that

i. NO_2 gas is brown, while NO is colorless.

ii. NO_2 gas is soluble in water while NO is insoluble.

iii. NO reacts with the oxygen of the air to form NO_2.

(b) *Many nonmetals,* such as S, P, C, and As. The products will be either NO or NO_2, H_2O, and either the acid or the insoluble acid anhydride.

$$S + 6\,NO_3^- + 4\,H^+ = SO_4^{--} + 6\,NO_2\uparrow + 2\,H_2O$$
$$C + 4\,NO_3^- + 4\,H^+ = CO_2\uparrow + 4\,NO_2\uparrow + 2\,H_2O$$
$$As + 5\,NO_3^- + 5\,H^+ = H_3AsO_4 + 5\,NO_2 + H_2O$$

(c) *A large number of reducing compounds* such as H_2S, H_2SO_3, Cl^-, Br^-, I^-, Fe^{++}, and Sn^{++}. The products are NO or NO_2, H_2O, and an oxidation product.

$$3\,H_2SO_3 + 2\,NO_3^- = 3\,SO_4^{--} + 2\,NO + H_2O + 4\,H^+$$
$$6\,I^- + 2\,NO_3^- + 8\,H^+ = 2\,NO + 3\,I_2 + 4\,H_2O$$
$$3\,Fe^{++} + NO_3^- + 4\,H^+ = 3\,Fe^{+++} + NO + 2\,H_2O$$

The last reaction is unique in that the NO combines with excess Fe^{++} ions to form the dark brown complex nitrosyliron(II) ion, $FeNO^{++}$; its formation is a very sensitive test for NO_3^- ions. In making the test, the unknown solution is first strongly acidified with concentrated H_2SO_4; $FeSO_4$ solution is then added. In the presence of NO_3^- ions, a brown ring due to $FeNO^{++}$ forms at the juncture of the two solutions.

Nitric acid oxidizes the protein in human skin to form a yellow substance known as *xanthoprotein*. This accounts for the yellow stain that is produced when concentrated nitric acid comes in contact with the skin.

(d) *Reaction of nitric acid with antimony and tin.* The "metals" antimony and tin react with concentrated HNO_3 in the unique manner indicated by the following equations:

$$2\,Sb + 10\,NO_3^- + 10\,H^+ = \mathbf{Sb_2O_5}\ \text{(white)} + 10\,NO_2\uparrow + 5\,H_2O$$
$$Sn + 4\,NO_3^- + 4\,H^+ = \mathbf{SnO_2}\ \text{(white)} + 4\,NO + 2\,H_2O$$

These reactions are similar to that shown by carbon [see (b), above] and suggest that tin and antimony are acting like nonmetals and that Sb_2O_5 and SnO_2 are insoluble acid anhydrides. The formation of these two insoluble acidic oxides illustrates the following general rules.

i. In the presence of an oxidizing agent an element which can exist in more than one oxidation state tends to go to a higher state. Therefore the oxide of Sn(IV) rather than that of Sn(II), and the oxide of Sb(V) rather than that of Sb(III) are formed.

ii. As the element goes to the higher of its several oxidation states, its oxide becomes more acidic and less basic (the element may be considered to become more nonmetallic and less metallic in character). Thus SnO is a typical basic oxide; SnO_2 is a typical acidic oxide. Likewise, Sb_2O_3 is predominantly basic, while Sb_2O_5 is acidic. The fact that, in its higher oxidation states, the oxides of an element are more acidic is illustrated by the following additional examples: H_2SO_4 is a stronger acid than H_2SO_3 because SO_3 is more acidic than SO_2; HNO_3 is a stronger acid than HNO_2 because N_2O_5 is more acidic than N_2O_3; H_3PO_4 is a stronger acid than H_3PO_3 because P_2O_5 is more acidic than P_2O_3; Cr(III) forms the metallic cation Cr^{+++}, while Cr(VI) behaves as a nonmetal and forms the anion CrO_4^{--}; Mn(II) forms the metallic cation Mn^{++}, while Mn(VII) acts like a typical nonmetal and forms the anion MnO_4^-.

iii. The basic oxides react with acids to form salts. Acidic oxides do not react with acids; if they react at all it is with water to form a solution of the acid. The less acidic the oxide of an element in groups IIIA, IVA, and VA, the less soluble it is in water. Tin and antimony are high-atomic-number members of groups IVA and VA, respectively. Therefore they are more metallic than nonmetallic in character. Therefore their high-oxidation-state oxides are weakly acidic, and hence very slightly soluble.

18.14 Commercial uses of nitric acid. It is used for the manufacture of nitrate fertilizers (chiefly NH_4NO_3), explosives, pyroxylin plastics, lacquers, dyes, and a variety of organic chemicals and inorganic salts.

Explosives such as nitroglycerine [$C_3H_5(NO_3)_3$], trinitrotoluene [TNT, $CH_3C_6H_2(NO_2)_3$], nitrocellulose [guncotton, smokeless powder $C_6H_7O_2(NO_2)_3$], and picric acid [$OHC_6H_2(NO_2)_3$], are prepared by treating glycerine [$C_3H_5(OH)_3$], toluene ($C_6H_5CH_3$), cellulose ($C_6H_{10}O_5$), and phenol (C_6H_5OH), respectively, with concentrated nitric acid in the presence of concentrated sulfuric acid. These explosives owe their effectiveness to the fact that they are very unstable and can be *detonated* by the shock generated by the explosion of such unstable *detonators* as mercury fulminate [$Hg(CNO)_2$] and lead azide [$Pb(N_3)_2$]. The instability of nitrogen compounds is probably due to the relative inactivity of nitrogen.

Black powder is a mixture of potassium nitrate, charcoal, and sulfur. It functions through rapid oxidation of the C and S by the KNO_3, with evolution of a large amount of heat, a mixture of CO, CO_2, SO_2, NO, NO_2, and N_2 being generated.

Questions and Problems

1. Give the detailed electronic configuration (*s*, *p*, *d*, and *f* electrons) of the nitrogen and bismuth atoms.

2. Arrange the group VA elements in the order of increasing: (a) atomic numbers; (b) atomic weights; (c) melting points; (d) boiling points; (e) densities; (f) atomic diameters; (g) electronegativity; (h) electropositivity; (i) nonmetallic character; (j) metallic character; (k) number of oxidation states.

3. Arrange the hydrides of the group VA elements in the order of: (a) decreasing stability; (b) increasing reducing power.

4. Arrange the oxides of the group VA elements in the order of: (a) decreasing acidic character; (b) increasing basic character; (c) decreasing solubility in water.

5. Indicate which is the more acidic oxide in each of the following pairs and give the reason for your choice: (a) N_2O_5 and N_2O_3; (b) P_2O_3 and P_2O_5; (c) N_2O_5 and P_2O_5; (d) SnO and SnO_2; (e) As_2O_5 and Sb_2O_5; (f) Bi_2O_3 and Bi_2O_5; (g) P_2O_5 and SO_3.

6. Indicate which is the stronger acid in each of the following pairs and give the reason for your choice: (a) H_3AsO_3 and H_3AsO_4; (b) H_3PO_4 and H_3AsO_4; (c) HNO_3 and HNO_2; (d) H_3PO_3 and H_2SO_3; (e) H_2SiO_3 and H_3PO_4.

7. Indicate which is the more water-soluble oxide in each of the following pairs and give the reason for your choice: (a) As_2O_5 and Sb_2O_5; (b) SiO_2 and P_2O_5.

8. Show by means of net equations how each of the following can be prepared in the laboratory: N_2, NH_3, HNO_3, NO, NO_2. Indicate how each is collected and make a sketch of the apparatus used in the preparation.

9. Describe the important commercial methods used for preparing each of the following and give equations for all reactions involved: (a) N_2; (b) NH_3; (c) HNO_3.

10. Define "nitrogen fixation." How is nitrogen "fixed"?

11. How could you distinguish between four colorless gases, one air, one N_2, one NH_3, and one NO?

12. How could you demonstrate that a solution of NH_3 in water is a weak base?

13. How could you determine, by all available methods, that dilute HNO_3 is a strong acid?

14. Given air, water, and coke as your raw materials, with any equipment that you need and unlimited supplies of heat and catalytic materials, point out, with the aid of necessary equations, how you could prepare NH_4NO_3.

15. List, and illustrate with appropriate equations, the chemical properties of: (a) NH_3; (b) HNO_3.

16. State the most important industrial uses of: (a) N_2; (b) NH_3; (c) HNO_3.

17. A tarnished copper crucible becomes bright, shiny copper-colored when heated in the presence of NH_3 gas. Explain.

18. Why is the Haber process for preparation of ammonia carried out at very high pressures, at moderate temperature, in the presence of a catalyst and with excess H_2?

19. Write net equations for the reaction of concentrated nitric acid with: (a) a metal; (b) a nonmetal; (c) a reducing compound.

20. The reacting system $4\ NH_3 + 5\ O_2 \rightleftarrows 4\ NO + 6\ H_2O$ + heat is in equilibrium in a closed container at 500°C. State how the equilibrium point will be affected by: (a) increasing the pressure; (b) increasing the temperature; (c) forcing more NH_3 into the system; (d) addition of platinum catalyst; (e) addition of HCl gas.

21. When Cu is treated in a flask with HNO_3, the evolved gas is brown. When this brown gas is bubbled through water and collected by displacement of water, the gas that is collected is colorless. When this colorless gas is exposed to air it turns brown. Explain, giving equations for all reactions.

22. How would you test for the presence of NO_3^- ions in a solution known to contain Na^+ as the only cation?

23. Why are the following statements or equations incorrect? Give the correct equation.

(a) The colorless gas was a mixture of NO and air.

(b) The hot brown gas was a mixture of NO_2 and SO_2.

(c) $Cu + 2\ HNO_3$ (excess conc) $= CuO + H_2O + 2\ NO$.

(d) Ammonia gas was prepared by heating NH_4Cl. The following reaction took place: $NH_4Cl \xrightarrow{\Delta} NH_3\uparrow + HCl$.

24. Explain, with the aid of equations, the following:

(a) A white deposit forms around the stoppers and vents of HCl, HNO_3, and NH_4OH reagent bottles when they are allowed to stand close together.

(b) Brown fumes are evolved when HNO_3 is heated.

(c) Brown fumes are evolved when concentrated HNO_3 is added to solid Na_2SO_3.

(d) A solution of $Zn(NO_3)_2$ reacts acidic to litmus paper.

25. When solid As, Sb, and Bi are treated with concentrated HNO_3, there are formed, respectively, a solution of H_3AsO_4, a white precipitate of Sb_2O_5, and a solution of Bi^{+++} ions. Account for the difference in behavior of the three.

26. Arrange the following in the order of decreasing hydrogen ion concentration: (a) 0.1 *M* HNO_2; (b) 0.1 *M* H_3PO_3; (c) 0.1 *M* HNO_3; (d) 0.1 *M* $NaNO_2$; (e) 0.1 *M* $NaNO_3$.

27. How many milliliters of 0.1 *N* HNO_3 will be required to react with 100 cc of a 22% solution of NH_3 in water whose density is 0.92 g/cc?

28. How many milliliters of 0.2 *N* $FeSO_4$ will be required to reduce the nitrate ion in 50 ml of 0.2 *M* HNO_3?

CHAPTER 19

Phosphorus

Phosphorus is one of the constituents of bones, teeth, and certain body proteins, and is therefore an important component of the foods that we eat. It is one of the elements absolutely necessary for the growth and development of plants, fruits, and grain. Since it is not present in soil in adequate amounts, it is one of the fertilizers that must be added to the soil. Radioactive P^{32} is proving to be effective in the treatment of leukemia and other blood diseases as well as certain types of skin cancer.

19.1 Occurrence. It is never found free in nature; it is too reactive. It constitutes 0.13% of the earth's crust, where it is found largely in deposits of *rock phosphate* [*phosphorite*, $Ca_3(PO_4)_2$] and *apatite* [$CaF_2 \cdot Ca_3(PO_4)_2$].

19.2 Commercial preparation. It is prepared by reduction of rock phosphate with coke and sand (SiO_2) in an electric furnace at a temperature of about 2000°C (see Figure 19.1). The following reactions take place.

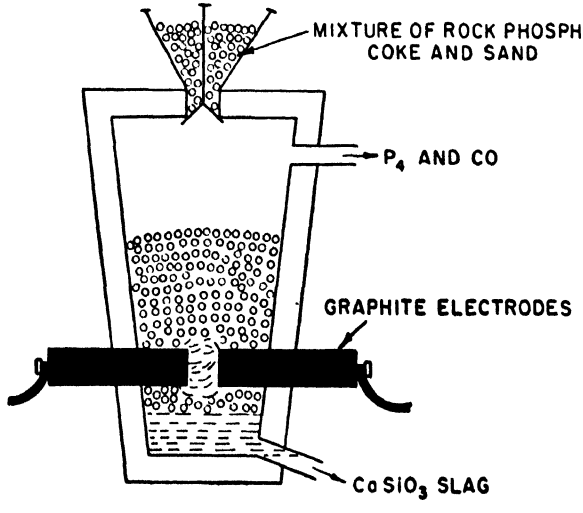


Figure 19.1. Electric furnace for the manufacture of phosphorus.

(1) $2\,Ca_3(PO_4)_2 + 6\,SiO_2$ (heated) $= 6\,CaSiO_3 + P_4O_{10}$

(2) $P_4O_{10} + 10\,C$ (heated) $= 10\,CO\uparrow + P_4\uparrow$

(3) P_4 (vapor) $= 4\,P$ (solid)

Equation (1) is of interest because it illustrates the replacement of a more volatile acidic oxide (P_4O_{10}) by a less volatile one (SiO_2).

Phosphorus vapor is a tetratomic molecule, P_4.

19.3 Physical properties (see Table 18.1). Its outstanding property is its existence in different *allotropic forms* (see 2.21), the most important of which are the *red* and the *white*. *White phosphorus* is a pale yellow, waxlike solid with a melting point of 44.1°C, a boiling point of 280°C, a density of 1.82 g/cc, and a kindling temperature of 30°C. It is soluble in carbon disulfide (CS_2) and is very poisonous. *Red phosphorus* is a nonpoisonous powder with a density of 2.34 and a kindling temperature of about 260°C. It is insoluble in CS_2 and sublimes at about 400°C. Both forms are insoluble in water.

19.4 Chemical properties

1. Phosphorus is a typical non-metal. It combines directly with hydrogen and with active metals to form phosphides. In these compounds it has its lowest oxidation state, −3.

$$2\,P + 3\,H_2 \text{ (heated)} = 2\,PH_3$$
$$3\,Ca + 2\,P = Ca_3P_2$$

In these reactions phosphorus, being the electronegative element, is the oxidizing agent.

2. It combines with oxygen to form P_2O_3 or P_4O_{10}. In these covalent oxides and in the compounds derived from them it has its higher oxidation numbers of +3 and +5.

$$4\,P + 3\,O_2 = 2\,P_2O_3 \text{ (in presence of excess phosphorus)}$$
$$4\,P + 5\,O_2 = P_4O_{10} \text{ (in presence of excess oxygen)}$$

Phosphorus, being the more electropositive element, is the reducing agent. In the presence of excess reducing agent, the phosphorus takes the lower oxidation number of +3, while in the presence of excess oxidizing agent it takes the higher number, +5.

3. It combines with sulfur and the halogens to form binary covalent compounds.

$$4\,P + 3\,S = P_4S_3$$
$$2\,P + 3\,I_2 = 2\,PI_3$$

19.5 Some important commercial uses. The most important uses are for the manufacture of phosphorus pentoxide, phosphoric acid, phosphorus sesquisulfide (P_4S_3), phosphor bronze, and matches.

Phosphoric acid is prepared by burning phosphorus in air and dissolving the P_4O_{10} in water.

$$4\ P + 5\ O_2 = P_4O_{10}$$
$$P_4O_{10} + 2\ H_2O = 4\ HPO_3 \text{ (metaphosphoric acid)}$$
$$HPO_3 + H_2O = H_3PO_4 \text{ (orthophosphoric acid)}$$

Phosphorus sesquisulfide is prepared by direct combination of phosphorus and sulfur.

$$4\ P + 3\ S \text{ (heated)} = P_4S_3$$

Phosphor bronze is an *alloy* containing copper, tin, and phosphorus (see 25.13).

19.6 Some important compounds and their uses

1. *Superphosphate*, $Ca(H_2PO_4)_2 + 2\ CaSO_4$ or $Ca(H_2PO_4)_2$, is the most important phosphorus fertilizer. It is prepared by treating ground rock phosphate with concentrated sulfuric acid or phosphoric acid.

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 = Ca(H_2PO_4)_2 + 2\ CaSO_4$$
$$Ca_3(PO_4)_2 + 4\ H_3PO_4 = 3\ Ca(H_2PO_4)_2$$

Since $Ca(H_2PO_4)_2$ is moderately soluble, the phosphorus which it contains is readily available for use by plants. Because $Ca_3(PO_4)_2$ is very insoluble, its phosphorus content is not readily available to plants.

A total of 11,111,000 tons of rock phosphate were mined in the United States in 1950 to be used largely in the manufacture of superphosphate. Florida produced about 78% of this total, Tennessee about 13%, and Idaho, Montana, Utah, and Wyoming together about 9%.

2. *Phosphoric acid.* It is used in the manufacture of superphosphate, other metal phosphates, and dental cement. It is manufactured by burning phosphorus in air and dissolving the oxide that is formed in water.

3. *Trisodium phosphate*, Na_3PO_4. It is used in cleansing agents, soaps, and washing powders.

4. *Phosphorus sesquisulfide*, P_4S_3. It is used in the manufacture of matches. A strike-anywhere type of match consists of (see Figure 19.2):

(a) *The tip.* It contains a substance (red phosphorus or P_4S_3) with a low kindling temperature, an oxidizing agent ($KClO_3$), and a glue or binder. When the match is struck on a rough surface, the heat of fric-

tion raises the P_4S_3 or red phosphorus to its kindling temperature and causes it to burst into flame. The oxidizing agent then causes rapid combustion to take place. This generates a large amount of heat.

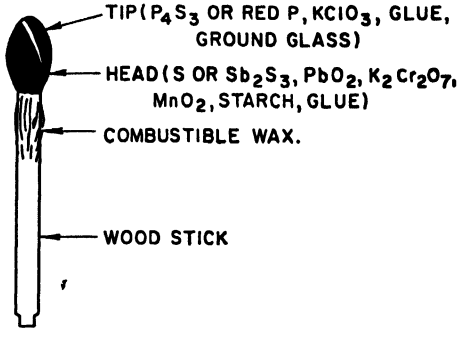


Figure 19.2. A strike-anywhere match.

(b) *The head.* It contains a combustible substance (S, Sb_2S_3) with a higher kindling temperature than red phosphorus or P_4S_3, an oxidizing agent (PbO_2, $K_2Cr_2O_7$, MnO_2), and a combustible binder (starch). The heat generated when the tip burns raises the S or Sb_2S_3 to its kindling temperature. The oxidizing agent promotes rapid combustion and causes the starch binder to be ignited. A large amount of heat is generated.

(c) *The stick.* It consists of a combustible material such as wood or paper. The heat generated when the head burns ignites the stick, which then continues to burn in the air.

Stated briefly, *friction ignites the tip, which ignites the head, which ignites the stick.*

In the safety match, the substances with low kindling temperature (red phosphorus and P_4S_3) are placed on the side of the box or holder rather than on the head of the match; the latter contains the oxidizing agent and the substances with higher kindling temperatures. To ignite the safety match it must be struck either on the side of the box or on some surface that is such a poor conductor of heat that the heat generated by friction accumulates to the point where the substances in the head are kindled.

5. *Phosphorus pentoxide,* P_4O_{10}. Because of its great affinity for water, with which it combines to form phosphoric acid, it is widely used as a drying agent and dehydrating agent.

19.7 Reactions involving the PO_4^{---} ion, H_3PO_4, and H_3PO_3

1. Identification of PO_4^{---} ion and H_3PO_4

(a) $3\,Ag^+ + PO_4^{---}$ (or H_3PO_4) = $\mathbf{Ag_3PO_4}$ (yellow; soluble in NH_4OH and in strong acids)

(b) $Mg^{++} + NH_4^+ + PO_4^{---} = \mathbf{MgNH_4PO_4}$ (white, crystalline, soluble in strong acids)

The solution to be tested is made alkaline with NH_4OH and is then treated with a solution of $MgCl_2$ containing NH_4Cl.

(c) $12\,MoO_4^{--} + 21\,H^+ + 3\,NH_4^+ + H_3PO_4 = 12\,H_2O + \mathbf{(NH_4)_3PO_4 \cdot 12\,MoO_3}$ (yellow; ammonium phosphomolybdate). The solution to be tested is made strongly acidic with nitric acid, heated, treated with a solution of ammonium molybdate $[(NH_4)_2MoO_4]$, and heated some more. The yellow precipitate forms slowly.

(d) $3\,Ba^{++} + 2\,PO_4^{---} = \mathbf{Ba_3(PO_4)_2}$ (white, soluble in HCl or HNO_3)

2. Reducing action of H_3PO_3

$$2\,MnO_4^- + 5\,H_3PO_3 + 6\,H^+ = 5\,H_3PO_4 + 2\,Mn^{++} + 3\,H_2O$$

This reaction of H_3PO_3 illustrates the rule that a compound in which an element exists in a lower of two or more oxidation states can function as a reducing agent.

3. Hydrolysis of phosphorus halides. This serves as a method for preparing HBr and HI (see 16.4).

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

Questions

1. Starting with rock phosphate as the only source of phosphorus and using any other necessary material and apparatus, show by means of equations how each of the following can be prepared: (a) P; (b) P_2O_3; (c) P_4O_{10}; (d) H_3PO_3; (e) H_3PO_4; (f) PBr_3; (g) P_4S_3; (h) PH_3; (i) Ag_3PO_4; (j) $MgNH_4PO_4$; (k) Mg_3P_2; (l) Superphosphate; (m) Na_3PO_4.

2. Point out what takes place when a strike-anywhere match is ignited. Write equations for all reactions.

3. Account for the fact that P_2O_3 is formed when phosphorus is burned in the presence of a limited supply of oxygen, while P_4O_{10} is formed when excess oxygen is present.

4. How could you distinguish between three colorless solutions containing, respectively, Cl^-, I^-, and PO_4^{---}?

5. Account for the fact that H_3PO_3 is a weaker acid than H_3PO_4 and that it can function as a reducing agent.

6. Account for the fact that a solution of Na_3PO_4 is quite strongly alkaline.

CHAPTER 20

Oxidation Potentials

20.1 When will an oxidation-reduction reaction take place? It was stated in Section 13.13 that nearly all reactions in solution fall in one of three classes, namely,

1. Simple replacement of an ion by a more reactive element
2. Direct combination of a cation with an anion
3. Oxidation of a constituent of one ion or molecule by another ion or molecule

In various sections of Chapters 16, 17, and 18 we noted the behaviors of a number of oxidizing agents and reducing agents and learned that:

1. To be able to act as an oxidizing agent, a substance must contain, in a higher oxidation state, an element which can exist in a lower oxidation state.

2. To be able to act as a reducing agent, a substance must contain, in a lower oxidation state, an element which can exist in a higher oxidation state.

3. Every oxidation-reduction reaction involves the reaction of an oxidizing agent with a reducing agent. In the course of the reaction the oxidation number of a component element of the oxidizing agent is decreased, while the oxidation number of a component element of the reducing agent is increased. The component element of the oxidizing agent whose oxidation number is decreased is said to be reduced. The component element of the reducing agent whose oxidation number is increased is said to be oxidized.

4. In the balanced equation for every oxidation-reduction reaction, the number of moles of oxidizing agent and reducing agent are such that the total increase in oxidation number of the element oxidized is exactly equal to the total decrease in oxidation number of the element reduced.

Looking back over these four statements, we find that we know pretty well how to identify potential oxidizing and reducing agents, we know how to interpret what happens when they react, and we know how to balance the equation for the reaction that takes place. But we recall that H_2SO_4 was able to oxidize HBr and HI, but was not able to oxidize HCl (see 16.2–10) and that HCl was able to reduce $KClO_3$ but was not able to reduce H_2SO_4, so we know that a given oxidizing agent will not

necessarily oxidize all potential reducing agents, and a given reducing agent will not necessarily reduce all potential oxidizing agents. So there arises a big and important question: How can we know whether or not a potential oxidizing agent will actually react with a potential reducing agent?

20.2 Driving force, free energy, change in free energy, and oxidation potential. As a start toward answering the question raised above, let us examine the two simple oxidation-reduction reactions represented by the following equations:



(1) $$Zn + Cu^{++} = Zn^{++} + Cu$$

(2) $$Cu + 2\,Ag^{+} = Cu^{++} + 2\,Ag$$

Each of these reactions is in reality the sum of two reactions. For reaction (1) the two equations representing the two component reactions are

(1a) $$Zn = Zn^{++} + 2e$$

(1b) $$Cu^{++} + 2e = Cu$$

If (a) and (b) are combined, the $2e$ on each side of the equality sign will cancel and we get the final equation,

$$Zn + Cu^{++} = Zn^{++} + Cu$$

This means that in the over-all process represented by equation (1), each zinc atom gives up 2 electrons to form zinc ions, and each copper ion picks up these 2 electrons to form copper atoms.

In similar fashion equation (2) can be resolved into

(2a) $$Cu = Cu^{++} + 2e$$

(2b) $$2\,Ag^{++} + 2e = 2\,Ag$$

We know from experimental observation that the reactions represented by equations (1) and (2) do take place; from Table 3.3, in which the metals are arranged in the order of their decreasing electropositivities, we can predict that they will take place in accordance with the empirical rule that a more electropositive metal will replace a less electropositive metal from a solution of its ions. By the *electropositivity* of a metal we mean the *driving force* with which the metal tends to give up its valence electrons (or electron) to form a cation. Thus the electropositivity of zinc means the driving force with which the reaction $Zn = Zn^{++} + 2e$ is impelled. If a driving force is to be exerted during a reaction, energy must be expended. That means that energy is ex-

pended when Zn changes to Zn^{++} in the reaction $Zn = Zn^{++} + 2e$. That in turn means that the effective energy content of the Zn^{++} ions must be less than that of the Zn atoms. The effective energy content of a system is referred to as the *free energy* of the system. [It should be noted that the free energy of a system is more than just the heat (energy) content; it is a summation or resultant or "product" of the heat content *and* the tendency for the heat energy to be expended or the probability that it will be expended. A system of lower heat content but higher tendency to expend this heat energy might well have a higher free energy than one with higher heat content but lower expending tendency. It is like a man with little money but much generosity being a greater potential source of contribution to charity than one with more money and little generosity.] The difference between the free energy of Zn and that of Zn^{++} is the *change in free energy* that occurs when the reaction $Zn = Zn^{++} + 2e$ takes place. This change in free energy provides the driving force of the reaction; it is what makes the reaction go, and is what is meant when we speak of the electropositivity of zinc.

Because the change in free energy provides the driving *force* of a reaction, it is referred to as a *potential;* and since the reactions with which we are now dealing all involve oxidation, it is referred to as the *oxidation potential* of the reaction. The oxidation potential represents, therefore, the change in free energy of a reaction; in the case of reactions involving metals it represents what we have been calling the electropositivity of the metal. The value of the oxidation potential is expressed in volts.

Tables 20.1 and 20.2 list the oxidation potentials of 87 common reactions in the order of decreasing potentials. The manner in which these values were determined will be discussed in Section 20.6.

20.3 Features of oxidation potentials. Before considering how oxidation potentials can be used to determine whether or not an oxidation-reduction reaction will take place, certain details regarding these potentials and the tables in which they are arranged should be clarified.

All values for $E°$ in the table are at 25°C. The concentration of each reactant which is in solution is 1 molal (1 mole of reactant in 1000 g of water). All gases are under a pressure of 1 atm. The potentials at other concentrations, temperatures, and pressures can be calculated in a manner which will not be considered in this book.

Note that all reactions are incomplete and reach a state of equilibrium as represented by the double arrows. The reason for this is obvious if we compare equations (1b) and (2a) in Section 20.2. When

zinc reacts with a solution of copper ions according to the equation $Zn + Cu^{++} = Zn^{++} + Cu$, the *half* of the equation (equation 1b) which represents the behavior of the copper ions is $Cu^{++} + 2e = Cu$. When copper reacts with a solution of silver ions according to the equation $Cu + 2\,Ag^{+} = Cu^{++} + 2\,Ag$, the *half* of the equation (equation 2a) which represents the behavior of the copper is $Cu = Cu^{++} + 2e$. It will be noted that equation (1b) is the reverse of (2a). The equation, $Cu \rightleftarrows Cu^{++} + 2e$, as given in these tables represents this reversibility; it tells us that under one set of conditions copper atoms will give up electrons to form copper ions, while under another set of conditions copper ions will pick up electrons to form copper atoms. The same thing applies to all 87 equations; they are all reversible, and depending on the conditions, can go either to the left or to the right.

Note that each one of the equilibrium reactions is set up so that electrons are given off when the reactants, on the left, react to form the products, on the right. This means that the substance on the left is being oxidized and is acting as a reducing agent. When the substance on the left acts as a reducing agent (reductant) the substance or substances on the right are formed as products. It follows that electrons must be taken up when the substances on the right react to form the substances on the left; this means that when the reaction goes to the left, the substance on the right is reduced, and this substance is acting as an oxidizing agent (oxidant). Stated briefly, when the reaction proceeds to the right the substance on the left is acting as a reducing agent; when it proceeds to the left the substance on the right is acting as an oxidizing agent.

The substance on the *left* at the *top* of the table is the *strongest reducing agent.* By analogous reasoning we conclude that the substance on the *left* at the *bottom* is the *weakest reducing agent.* As we go from top to bottom, the substances on the left become weaker and weaker reducing agents. That means that the lower the oxidation potential, the weaker the reducing ability of the reducing agent on the left.

The substance on the *right* at the *bottom* of a table is the *strongest oxidizing agent.* The substance on the *right* at the *top* is the *weakest* oxidizing agent. As we go from top to bottom, the *oxidizing ability* of the substance on the right becomes stronger and stronger. That means that the lower the oxidation potential, the stronger the oxidizing ability of the oxidizing agent on the right.

20.4 Use of oxidation potentials to determine whether or not a reaction will take place. In any table of oxidation potentials such as Tables 20.1 and 20.2 *an oxidizing agent with a lower potential will*

TABLE 20.1

STANDARD OXIDATION POTENTIALS IN ACID SOLUTION

	Reaction	*Potential, E°* (in volts)
1.	$K \rightleftarrows K^+ + e^-$	2.925
2.	$Ba \rightleftarrows Ba^{++} + 2e^-$	2.90
3.	$Ca \rightleftarrows Ca^{++} + 2e^-$	2.87
4.	$Na \rightleftarrows Na^+ + 2e^-$	2.714
5.	$Mg \rightleftarrows Mg^{++} + 2e^-$	2.37
6.	$Al \rightleftarrows Al^{+++} + 3e^-$	1.66
7.	$Mn \rightleftarrows Mn^{++} + 2e^-$	1.18
8.	$Zn \rightleftarrows Zn^{++} + 2e^-$	0.763
9.	$Cr \rightleftarrows Cr^{+++} + 3e^-$	0.74
10.	$H_2Te \rightleftarrows Te + 2\,H^+ + 2e^-$	0.72
11.	$AsH_3 \rightleftarrows As + 3\,H^+ + 3e^-$	0.60
12.	$H_3PO_2 + H_2O \rightleftarrows H_3PO_3 + 2\,H^+ + 2e^-$	0.50
13.	$Fe \rightleftarrows Fe^{++} + 2e^-$	0.440
14.	$Cr^{++} \rightleftarrows Cr^{+++} + e^-$	0.41
15.	$Cd \rightleftarrows Cd^{++} + 2e^-$	0.403
16.	$H_2Se \rightleftarrows Se + 2\,H^+ + 2e^-$	0.40
17.	$Pb + SO_4^{--} \rightleftarrows PbSO_4 + 2e^-$	0.356
18.	$Co \rightleftarrows Co^{++} + 2e^-$	0.277
19.	$H_3PO_3 + H_2O \rightleftarrows H_3PO_4 + 2\,H^+ + 2e^-$	0.276
20.	$Ni \rightleftarrows Ni^{++} + 2e^-$	0.250
21.	$Sn \rightleftarrows Sn^{++} + 2e^-$	0.136
22.	$Pb \rightleftarrows Pb^{++} + 2e^-$	0.126
23.	$HS_2O_4^- + 2\,H_2O \rightleftarrows 2\,H_2SO_3 + H^+ + 2e^-$	0.08
24.	$H_2 \rightleftarrows 2\,H^+ + 2e^-$	0.000
25.	$HClO + H_2O \rightleftarrows HCOOH + 2\,H^+ + 2e^-$	-0.056
26.	$PH_3 \rightleftarrows P + 3\,H^+ + 3e^-$	−0.06
27.	$2\,S_2O_3^{--} \rightleftarrows S_4O_6^{--} + 2e^-$	−0.08
28.	$H_2S \rightleftarrows 2\,H^+ + S + 2e^-$	−0.141
29.	$Sn^{++} \rightleftarrows Sn^{++++} + 2e^-$	−0.15
30.	$H_2SO_3 + H_2O \rightleftarrows SO_4^{--} + 4\,H^+ + 2e^-$	−0.17
31.	$2\,Hg + 2\,Cl^- \rightleftarrows Hg_2Cl_2 + 2e^-$	−0.2676
32.	$Cu \rightleftarrows Cu^{++} + 2e^-$	−0.337
33.	$S + 3\,H_2O \rightleftarrows H_2SO_3 + 4\,H^+ + 4e^-$	−0.45
34.	$2\,I^- \rightleftarrows I_2 + 2e^-$	−0.5355
35.	$H_3AsO_3 + H_2O \rightleftarrows H_3AsO_4 + 2\,H^+ + 2e^-$	−0.559
36.	$MnO_4^{--} \rightleftarrows MnO_4^- + e^-$	−0.564
37.	$H_2O_2 \rightleftarrows O_2 + 2\,H^+ + 2e^-$	−0.682
38.	$Fe^{++} \rightleftarrows Fe^{+++} + e^-$	−0.771
39.	$Ag \rightleftarrows Ag^+ + e^-$	−0.7991
40.	$NO_2 + H_2O \rightleftarrows NO_3^- + 2\,H^+ + e^-$	−0.80
41.	$Hg \rightleftarrows Hg^{++} + 2e^-$	−0.854
42.	$NO + 2\,H_2O \rightleftarrows NO_3^- + 4\,H^+ + 3e^-$	−0.96
43.	$NO + H_2O \rightleftarrows HNO_2 + H^+ + e^-$	−1.00
44.	$I^- + H_2O \rightleftarrows HIO + H^+ + 2e^-$	−1.00
45.	$2\,Br^- \rightleftarrows Br_2\,(aq) + 2e^-$	−1.065
46.	$H_2SeO_3 + H_2O \rightleftarrows SeO_4^{--} + 4\,H^+ + 2e^-$	−1.15
47.	$2\,H_2O \rightleftarrows O_2 + 4\,H^+ + 4e^-$	−1.229

Table 20.1 (Cont.)

	Reaction	*Potential, E°* (in volts)
48.	$Mn^{++} + 2\ H_2O \rightleftarrows MnO_2 + 4\ H^+ + 2e^-$	−1.23
49.	$2\ Cr^{+++} + 7\ H_2O \rightleftarrows Cr_2O_7^{--} + 14\ H^+ + 6e^-$	−1.33
50.	$2\ Cl^- \rightleftarrows Cl_2\ (aq) + 2e^-$	−1.3595
51.	$Cl^- + 3\ H_2O \rightleftarrows ClO_3^- + 6\ H^+ + 6e^-$	−1.45
52.	$Pb^{++} + 2\ H_2O \rightleftarrows PbO_2 + 4\ H^+ + 2e^-$	−1.455
53.	$Cl^- + H_2O \rightleftarrows HClO + H^+ + 2e^-$	−1.49
54.	$Mn^{++} + 4\ H_2O \rightleftarrows MnO_4^- + 8\ H^+ + 5e^-$	−1.51
55.	$Ce^{+++} \rightleftarrows Ce^{++++} + e^-$	−1.61
56.	$PbSO_4 + 2\ H_2O \rightleftarrows PbO_2 + SO_4^{--} + 4\ H^+ + 2e^-$	−1.685
57.	$MnO_2 + 2\ H_2O \rightleftarrows MnO_4^- + 4\ H^+ + 3e^-$	−1.695
58.	$Bi^{+++} + 3\ H_2O \rightleftarrows HBiO_3 + 5\ H^+ + 2e^-$	−1.70
59.	$2\ H_2O \rightleftarrows H_2O_2 + 2\ H^+ + 2e^-$	−1.77
60.	$Co^{++} \rightleftarrows Co^{+++} + e^-$	−1.82
61.	$2\ SO_4^{--} \rightleftarrows S_2O_8^{--} + 2e^-$	−1.91
62.	$O_2 + H_2O \rightleftarrows O_3 + 2\ H^+ + 2e^-$	−2.07
63.	$2\ F^- \rightleftarrows F_2 + 2e^-$	−2.65
64.	$2\ HF\ (aq) \rightleftarrows F_2 + 2\ H^+ + 2e^-$	−3.06

Table 20.2

Standard Oxidation Potentials in Alkaline Solution

	Reaction	*Potential, E°* (in volts)
65.	$K \rightleftarrows K^+ + e^-$	2.925
66.	$Al + 4\ OH^- \rightleftarrows Al(OH)_4^- + 3e^-$	2.35
67.	$HPO_3^- + 3\ OH^- \rightleftarrows PO_4^{---} + 2\ H_2O + 1e^-$	1.12
68.	$S_2O_4^{--} + 4\ OH^- \rightleftarrows 2\ SO_3^{--} + 2\ H_2O + 2e^-$	1.12
69.	$CN^- + 2\ OH^- \rightleftarrows CNO^- + H_2O + 2e^-$	0.97
70.	$SO_3^{--} + 2\ OH^- \rightleftarrows SO_4^{--} + H_2O + 2e^-$	0.93
71.	$Sn(OH)_4^{--} + 2\ OH^- \rightleftarrows Sn(OH)_6^{--} + 2e^-$	0.90
72.	$Sn + 4\ OH^- \rightleftarrows Sn(OH)_4^{--} + 2e^-$	0.76
73.	$Cr(OH)_4^- + 4\ OH^- \rightleftarrows CrO_4^{--} + 4\ H_2O + 3e^-$	0.48
74.	$H_2O_2 + 2\ OH^- \rightleftarrows O_2 + 2H_2O + 2e^-$	0.076
75.	$Mn(OH)_2 + 2\ OH^- \rightleftarrows MnO_2 + H_2O + 2e^-$	0.05
76.	$Cu(NH_3)_2^+ + 2\ NH_3 \rightleftarrows Cu(NH_3)_4^{++} + e^-$	0.0
77.	$Co(NH_3)_6^{++} \rightleftarrows Co(NH_3)_6^{+++} + e^-$	-0.1
78.	$Co(OH)_2 + OH^- \rightleftarrows Co(OH)_3 + e^-$	-0.17
79.	$4\ OH^- \rightleftarrows O_2 + 2\ H_2O + 4e^-$	-0.401
80.	$I^- + 2\ OH^- \rightleftarrows IO^- + H_2O + 2e^-$	−0.49
81.	$Ni(OH)_2 + 2\ OH^- \rightleftarrows NiO_2 + 2\ H_2O + 2e^-$	−0.49
82.	$MnO_4^{--} \rightleftarrows MnO_4^- + e^-$	−0.54
83.	$MnO_2 + 4\ OH^- \rightleftarrows MnO_4^- + 2\ H_2O + 3e^-$	−0.57
84.	$MnO_2 + 4\ OH^- \rightleftarrows MnO_4^{--} + 2\ H_2O + 2e^-$	−0.60
85.	$Br^- + 2\ OH^- \rightleftarrows BrO^- + H_2O + 2e^-$	−0.76
86.	$2\ OH^- \rightleftarrows H_2O_2 + 2e^-$	−0.88
87.	$O_2 + 2\ OH^- \rightleftarrows O_3 + H_2O + 2e^-$	−1.24

oxidize any reducing agent with a higher potential. A reducing agent with a higher potential will reduce any oxidizing agent with a lower potential. That means that at 25°C, in 1 molal solution, at a pressure of 1 atm, *any substance on the right* in Tables 20.1 and 20.2 *will oxidize* (will be reduced by) *any substance above it* and *on the left. Any substance on the left will reduce* (will be oxidized by) *any substance below it* and *on the right.* A substance on the left will not reduce (be oxidized by) a substance above it and on the right. A substance on the right will not oxidize (be reduced by) a substance below it and on the left.

To illustrate the application of these rules: The potential of the reaction, $Zn = Zn^{++} + 2e$ (equation 8) is higher (0.763 volt) than that of the reaction, $Ag = Ag^{+} + e$ (equation 39, −0.7991 volt). Therefore Zn will be oxidized to Zn^{++} by Ag^{+}; the Ag^{+} will be reduced to Ag by Zn. The reaction that takes place will be

$$Zn + 2\,Ag^{+} = Zn^{++} + 2\,Ag$$

This is equivalent to saying that zinc will *replace* Ag^{+} ions from solution. It should be noted again that the reaction $Zn + 2\,Ag^{+} = Zn^{++} + 2\,Ag$ is the sum of the two reactions $Zn = Zn^{++} + 2e$ and $2\,Ag^{+} + 2e = 2\,Ag$. Each of the two parts is referred to as a *half reaction.* In this respect all the reactions given in Tables 20.1 and 20.2 are referred to as *half reactions.*

Ferric ion (equation 38) is an oxidizing agent, Fe^{++} is a reducing agent; Fe^{+++} will oxidize I^{-} to I_2 (equation 34) but will not oxidize Br^{-} to Br_2 (equation 45) or Cl^{-} to Cl_2 (equation 50). Ferrous ion (equation 38) will reduce Cl_2 to Cl^{-} (equation 50) and Br_2 to Br^{-} (equation 45) but will not reduce I_2 to I^{-} (equation 34).

Iodide ion (equation 34) will be oxidized to I_2 by HNO_2 (equation 43). The equation for the reaction will be

$$2\,I^{-} + 2\,HNO_2 + 2\,H^{+} = I_2 + 2\,NO + 2\,H_2O$$

Iodide ion will be oxidized to I_2 by all the oxidizing agents on the right side of equations 35 to 64. Ferric ion will be reduced to Fe^{++} by all the reducing agents on the left side of equations 1 to 37. Ferrous ion (equation 38) is readily oxidized to Fe^{+++} in acid solution by $Cr_2O_7^{--}$ (equation 49), MnO_4^{-} (equation 54), and Ce^{+++} (equation 55). When an acid solution of bismuthate ($HBiO_3$, equation 58) is treated with an acid solution of Mn^{++} (equation 54) the following reaction will take place.

$$5\,HBiO_3 + 2\,Mn^{++} + 9\,H^{+} = 5\,Bi^{+++} + 2\,MnO_4^{-} + 7\,H_2O$$

Hydrogen sulfide (equation 28) will reduce $Cr_2O_7^{--}$ to Cr^{+++} (equation 49), MnO_4^- to Mn^{++} (equation 54), and NO_3^- to NO (equation 42).

Sulfurous acid (equation 30) will be oxidized to SO_4^{--} by each of the following solutions commonly available in the laboratory: NO_3^- (equations 40 and 42), I_2 (equation 34), HIO (equation 44), Br_2 (equation 45), Cl_2 (equation 50), $Cr_2O_7^{--}$ (equation 49), ClO_3^- (equation 51), HClO (equation 53), MnO_4^- (equation 54), and H_2O_2 (equation 59).

Fluorine (equation 64) is the most powerful oxidizing agent, but among the common oxidizing agents available in the laboratory, $S_2O_8^{--}$ (equation 61), H_2O_2 (equation 59), and MnO_4^- (equations 54 and 57) are the strongest. Hydrogen peroxide is unique in that, even though it is the most powerful of the common oxidizing agents (equation 59) it can, under proper conditions, function as a fairly strong reducing agent as illustrated in equation (37).

Hydrogen telluride, H_2Te (equation 10) is a stronger reducing agent than H_2Se (equation 16), which is stronger than H_2S (equation 28); this is in line with what was learned in Chapter 17, namely, that as the atomic number of the element in group VIA increases, the stability of the hydrogen compound decreases and its reducing power increases.

It should be pointed out that the oxidation potentials give no information about the rate at which a reaction between two substances will occur.

As already noted, the potential of a specific reaction will vary with change of temperature and concentration of the oxidant or reductant. As the concentration of a reducing solution increases, the potential of the reducing agent increases; likewise, as the concentration of an oxidizing agent increases, its potential decreases. Increase in temperature generally increases the potential of a reducing agent and decreases the potential of an oxidizing agent. For these reasons reactions may occur at higher temperatures and concentrations which, according to Tables 20.1 and 20.2, would not take place. Thus hot concentrated H_2SO_4 will oxidize iodides and HI to iodine and bromides and HBr to bromine, even though Table 20.1 shows that both iodine solution (equation 34) and bromine solution (equation 45) will oxidize H_2SO_3 to SO_4^{--} (equation 30). A molal solution of Cl^- ion (equation 49) will not be oxidized to Cl_2 by MnO_2 (equation 48); however, concentrated HCl is readily oxidized by MnO_2.

20.5 Calculation of the potential of an oxidation-reduction reaction. *The potential of a reaction is the algebraic difference of the potentials of the two half reactions.* Thus a battery consisting of zinc in

contact with 1 molal $ZnSO_4$, and copper in contact with 1 molal $CuSO_4$ at 25°C, will develop a potential of about 1.1 volts. The potential ($E°$) of the reaction $Zn = Zn^{++} + 2e$ is +0.763 volt, and of the reaction $Cu^{++} + 2e = Cu$ is −0.337 volt. The voltage of the couple is $+0.763 - (-0.337) = 1.100$ volts. (See 25.13, page 461, for a detailed discussion of the reactions that take place in typical batteries.)

For a cell in which the over-all reaction is

$$Zn + Sn^{++} = Zn^{++} + Sn$$

the voltage is 0.627 volt. For the half reaction, $Zn = Zn^{++} + 2e$, potential $E°$ is 0.763 volt. For the half reaction, $Sn^{++} + 2e = Sn$, potential $E° = 0.136$ volt; $0.763 - 0.136 = 0.627$.

For the reaction represented by the equation

$$2\,Al + 3\,Zn^{++} = 2\,Al^{+++} + 3\,Zn$$

the voltage is 0.897 volt. The value of $E°$ for the half reaction $Al = Al^{+++} + 3e^-$ is 1.66 volts, while $E°$ for the reaction $Zn^{++} + 2e^- = Zn$ is 0.763 volt; $1.66 - 0.763 = 0.897$. It should be noted that, even though, in this illustration, it is necessary to take 2 gram-atoms of aluminum and 3 gram-ions of zinc ions to balance the equation, the potential is the same as if 1 gram-atom of each were involved. Potential is a measure of the force with which electrons are expelled per equivalent and is independent of the number of atoms or ions that are present.

The reaction $2\,Fe^{+++} + Sn^{++} = 2\,Fe^{++} + Sn^{++++}$ will develop a voltage of 0.621 volt when the concentrations are 1 molal. Potential $E°$ for the reaction $Fe^{++} = Fe^{+++} + e^-$ is −0.77, while for the reaction $Sn^{++} = Sn^{++++} + 2e^-$, its value is −0.15; $-0.15 - (-0.771) = 0.621$.

The two half reactions in the ordinary lead storage battery are

(Eq. 17) $Pb + SO_4^{--} = PbSO_4 + 2e$ $\qquad E° = 0.356$ v

(Eq. 56) $PbO_2 + SO_4^{--} + 2\,H^+ = PbSO_4 + 2\,H_2O$ $\qquad E° = -1.685$ v

The theoretical voltage of the battery is $0.356 - (-1.685) = 2.031$ volts.

20.6 Determination of oxidation potentials. The potentials ($E°$ values) of most of the half reactions given in Table 20.1 have been calculated from either the standard free energies of the substances involved, the equilibrium constant of the half reaction, or the heats of formation of the substances involved. The calculations are too complicated to be considered in an elementary textbook.

The potentials ($E°$ values) of a fairly large number of the reactions have been obtained by direct experimental measurements of the voltages developed

when the reactants are the components of a battery. In this method also, calculations are necessary to obtain the E° values from the experimental values.

To help get a better picture of what is meant by oxidation potential and to point out the use of the reaction $H = H^+ + e$ as a reference standard, let us assume, for the purpose of the explanation that follows, that we have an ideal system and that the measurements that are made do in fact give the correct values for the potential of a reaction. Under such conditions the oxidation potential of the reaction $Zn = Zn^{++} + 2e$ can be determined by direct measurement of the voltage in the following manner: A sheet of pure zinc is attached, by means of a length of copper wire, to one pole of a voltmeter. A special type of platinum electrode constructed in such a way that it can be kept surrounded by a film of hydrogen gas is attached to the other pole of the meter by another length of copper wire. We will call this platinum electrode the *hydrogen electrode*. The sheet of zinc and the hydrogen electrode are then dipped into 1 molal HCl. The voltmeter immediately registers a reading of about 0.75 volt. This voltage is the net result of the following reactions: At the sheet of zinc, zinc metal goes into solution to form zinc ions. In this conversion of zinc to Zn^{++} two electrons are given off: $Zn = Zn^{++} + 2e^-$. The electrons are picked up by the zinc sheet and move along the copper wire through the voltmeter. This movement of electrons is called *electric current*. The electrons finally move all the way around through the copper wire to the hydrogen electrode. The H^+ ions in the 1 molal HCl are attracted by the electrons that have gathered on the hydrogen electrode. As a result they move to the hydrogen electrode, where each picks up an electron and is thereby converted to a hydrogen atom, and finally to H_2 gas. The reaction that takes place may be represented by the equation $2\ H^+ + 2e^- = H_2$. The over-all reaction at the two electrodes can be represented by the equation $Zn + 2\ H^+ \rightleftarrows Zn^{++} + H_2$. It is this over-all reaction that is responsible for the flow of current and hence for the voltage. The setup that has been described is called a *battery*. Since the reaction $Zn = Zn^{++} + 2e^-$ takes place in one half of the battery, and the reaction $2\ H^+ + 2e^- = H_2$ takes place in the other half, each separate reaction is referred to as a *half reaction*. The reaction $Zn = Zn^{++} + 2e$ represents *oxidation* of Zn to Zn^{++}. The reaction $2\ H^+ + 2e = H_2$ represents *reduction* of H^+ to H_2. Therefore the over-all reaction is an *oxidation-reduction* reaction.

The question will now arise, If zinc gives off electrons and forms Zn^{++} ions in the manner represented by the equation $Zn = Zn^{++} + 2e^-$, why does not hydrogen also give off electrons to form H^+ ions in the manner represented by the equation $H_2 = 2\ H^+ + 2e^-$? As a matter of fact, hydrogen does tend to give off electrons to form H^+ ions, but the driving "force" with which zinc gives off electrons is so much greater than the "force" with which hydrogen gives off electrons, that when zinc and hydrogen are paired up in a battery, the hydrogen is in a sense overpowered by the zinc and has no chance to give off electrons. What happens when the sheet of zinc and the hydrogen electrode, connected by the copper wire, are dipped into the HCl is this: As soon as they enter, each one tries to generate electrons and send them along the copper wire. The H_2 tries to react $H_2 = 2\ H^+ + 2e^-$ and send electrons in one direction, while the Zn tries

to react $Zn = Zn^{++} + 2e^-$, and send electrons in the opposite direction. The zinc gives off its electrons with so much more force than the hydrogen emits its electrons that the hydrogen-generated electrons are, essentially, forced back out of the wire. Instead of the reaction going $H_2 = 2\,H^+ + 2e^-$, it actually goes $2\,H^+ + 2e^- = H_2$, the H^+ ions in the latter reaction coming from the solution in the manner already explained. However, during the entire operation of the battery, the H_2 never quits trying to give off electrons; it never quits trying to realize the reaction $H_2 = 2\,H^+ + 2e^-$.

Suppose that the force with which zinc gives off electrons has a value that is equal to, let us say, 2.60 units, and the "force" with which hydrogen gives off electrons is 1.85 units; then, as long as the cell is operating, zinc will be sending electrons along the wire with a force of 2.60 units, and hydrogen will be trying to send back electrons in the opposite direction with a force of 1.85 units. Because the zinc-generated electrons exert a greater force, they are the ones that will move along the wire, but the actual "force" with which they move will be the difference between the force with which they are pushed by the zinc and opposed by the hydrogen. This is the difference between 2.60 and 1.85, or 0.75. This difference is the *voltage* or *electromotive force* (emf) of the battery.

Suppose we decide, arbitrarily, to call the force with which hydrogen gives off electrons zero. Then, since we find by actual measurement that the voltage of the $Zn + 2\,H^+ \rightleftarrows Zn^{++} + H_2$ reaction is 0.75, that means that by comparison with the force with which hydrogen gives off electrons the force or potential with which zinc gives off electrons is 0.75. This value, 0.75 volt, is then the experimentally determined value of the oxidation potential of the reaction $Zn = Zn^{++} + 2e$. To call the potential of the reaction $H_2 = 2\,H^+ + 2e^-$ zero does not imply that H_2 has no tendency to give off electrons. It simply means that this tendency is going to be *called* zero. We can then use it as a standard reference point for determining the potentials of all other half reactions.

If cadmium were to be substituted for zinc, the voltmeter would register a potential of 0.403 volt, while if tin were used, the potential would be 0.14 volt. That means that the oxidation potential of the reaction $Cd = Cd^{++} + 2e^-$ is 0.403 volt, while the oxidation potential of the reaction $Sn = Sn^{++} + 2e^-$ is 0.14 volt.

If copper is substituted for zinc and 1 molal $CuCl_2$ is substituted for HCl, a very interesting thing happens. Current flows, and the voltmeter registers a voltage of about 0.34, but the electrons can now be shown to be moving in the wire away from the hydrogen electrode rather than toward it. This means that the reaction at the hydrogen electrode is $H_2 = 2\,H^+ + 2e^-$, while the reaction at the copper electrode is $Cu^{++} + 2e^- = Cu$. This means that the potential of the half reaction $H_2 = 2\,H^+ + 2e^-$, is 0.34 volt *greater* than the potential of the half reaction $Cu = Cu^{++} + 2e^-$. Another way to put it would be to use the potential of the reaction $H_2 = 2\,H^+ + 2e^-$ as a standard and say that the potential of the half reaction $Cu = Cu^{++} + 2e^-$ is 0.337 volt *less* than the potential of the reaction $H_2 = 2\,H^+ + 2e^-$. Even more simply, we can say that the potential of the half reaction $Cu = Cu^{++} + 2e^-$ is -0.337 volt, meaning thereby that

its potential is 0.337 *less* than the voltage of the standard half reaction, $H_2 = 2\,H^+ + 2e^-$.

20.7 When will a reaction occur between ions? In Section 13.3 we faced the question, How can we know whether or not a reaction will take place when two electrolytes are brought together in solution, and if they do react, what the products will be? We learned, in that section, the rules that enable us to determine when a cation will combine directly with an anion. In this chapter we have learned how, with the aid of a table of oxidation potentials, we can determine whether or not replacement or other oxidation-reduction reactions will take place. That means that, aided by Tables 11.2, 11.3, 20.1 and 20.2, and the list of strong and weak electrolytes given in Section 12.4, we are now equipped to decide what, if anything, will happen when any two electrolytes are brought together in solution.

Oxidation Potentials, 2d ed., by W. H. Latimer, Prentice-Hall, Inc., New York, 1952, should be consulted for a complete discussion of oxidation potentials.

Questions and Problems

1. Select from the following list of compounds and ions: (a) those whose solutions can function as oxidizing agents; (b) those whose solutions can function as reducing agents.

Using these substances as oxidants and reductants, write net equations for 10 oxidation-reduction reactions. Do not use the same oxidant or reductant in more than one reaction. If a substance will function as both oxidant and reductant it can be used in two reactions. Note whether each reaction is to be carried out in acid or alkaline solution. H_2SO_3, MnO_4^-, Fe^{+++}, Fe^{++}, $Cr_2O_7^{--}$, Sn^{++}, I^-, H_3PO_3, H_2O_2, $HS_2O_4^{--}$, $Sn(OH)_4^{--}$, HIO, HNO_2, H_3AsO_3, $HBrO_3$, Cl^-, $S_2O_8^{--}$, ClO_3^-, H_2SeO_3, BrO^-, I_2 (aq), H_2S, NO_3^-, H_3AsO_4, Ce^{++++}, HCHO, H_2Se, H_2PO_2, Mn^{++}, Co^{+++}, O_3 (ozone), O_2.

2. Account for the following facts.

(a) The substance $Co(OH)_3$ is fairly stable in alkaline solution but is readily reduced to Co(II) in acid solution.

(b) Hydrogen peroxide readily reduces Cr(VI) in acid solution but not in alkaline solution.

(c) When $Mn(OH)_2$ in alkaline solution is exposed to the air, it is oxidized to black MnO_2, but when Mn^{++} in acid solution is exposed to the air, oxidation to MnO_2 does not take place.

3. Calculate the theoretical voltage developed by batteries in which each of the following reactions is taking place (solutions are 1 molal at 25°C).

(a) $Mg + 2\,Ag^{+} = Mg^{++} + 2\,Ag$.

(b) $2\,Al + 3\,Cu^{++} = 2\,Al^{+++} + 3\,Cu$.

CHAPTER 21

Carbon, Carbon Monoxide, Carbon Dioxide

21.1 The properties of the group IVA elements. The group IVA elements show the same sort of decrease in nonmetallic character and increase in metallic character with increase in atomic number that has already been noted for the elements of groups VA, VIA, and VIIA. In line with the fact that, in moving to the left in the periodic table, the elements in a period become less nonmetallic, less electronegative, and more metallic, the group IVA elements are uniformly less nonmetallic and less electronegative than the elements in corresponding periods in group VA.

The decrease in nonmetallic character of the group IVA elements with increase in atomic number is shown in the following ways.

1. The oxides of C and Si are acidic, while the oxides of Ge, Sn, and Pb are amphoteric.

2. The elements C and Si form weak acids, while Ge, Sn, and Pb form amphoteric hydroxides.

3. Carbon forms a very large number of stable binary hydrogen compounds; silicon also forms many such compounds but fewer than carbon. Germanium forms three unstable hydrides. Tin forms one very unstable hydride, while the existence of a hydride of lead is open to question.

4. The chloride of carbon is so nonpolar that it is insoluble in water; $SiCl_4$ hydrolyzes in the fashion of the chloride of a nonmetal to yield silicic and hydrochloric acids. The chlorides of Ge, Sn, and Pb ionize to give cations and chloride ions in the characteristic fashion of chlorides of metals.

5. Carbon and silicon have oxidation states of -4, -2, 2, and 4, while germanium, tin, and lead have states of 2 and 4.

6. Carbon, and to a lesser extent, silicon combine with metals to form salts (carbides and silicides). Germanium shows some tendency to form binary salts with active metals; tin and lead do not combine with metals.

7. Lead, tin, and germanium react with solutions of salts of metals

TABLE 21.1

THE GROUP IVA ELEMENTS

Element	Period	At. no.	At. wt	At. diam.	Configuration	Density	Mp	Bp	Color and state	Electric cond	Oxidation states	Character of oxide
Carbon	2	6	12.01	1.54	2, 4	2.25	sublimes 3500°	—	silver-gray, brittle, solid	good	−4, 2, 4	acidic
Silicon	3	14	28.06	2.35	2, 8, 4	2.40	1430°	2600°	silver-gray, brittle, solid	poor	−4, 2, 4	acidic
Germanium	4	32	72.60	2.45	2, 8, 18, 4	5.36	960°	2700°	gray, brittle, crystalline, metallic	fair	2, 4	amphoteric
Tin	5	50	118.70	2.82	2, 8, 18, 18, 4	7.31	232°	2260°	silver-gray, metal	good	2, 4	amphoteric
Lead	6	82	207.21	3.08	2, 8, 18, 32, 18, 4	11.34	327°	1744°	silver-gray, metal	good	2, 4	amphoteric

of lower oxidation potential to form Pb^{++}, Sn^{++}, and Ge^{++} ions. Carbon and silicon do not displace metals from solutions of their salts.

8. Germanium, tin, and lead have the characteristic luster of metals; carbon and silicon do not.

9. There is an increase in electric conductivity of the solid element in going from silicon to germanium, tin, and lead. Carbon is unique among nonmetals in that one of its allotropic forms, graphite, has a high electric conductivity.

Because of their characteristically metallic character, tin and lead will be considered along with the other metals in the latter section of this book. Silicon will be discussed in more detail in Chapter 23. Germanium will be given brief mention in Chapter 36.

21.2 Natural occurrence of carbon

1. It is widely distributed in the free state as coal, graphite, and diamond.

2. In the combined state it occurs as metal carbonates (limestone, $CaCO_3$; marble, $CaCO_3$; magnesite, $MgCO_3$; dolomite, $MgCO_3 \cdot CaCO_3$; siderite, $FeCO_3$; malachite, $CuCO_3 \cdot Cu(OH)_2$); hydrocarbons (methane, CH_4; natural gas; petroleum), carbohydrates (starch, cellulose, sugars), fats (tallow and other animal fats), oils (cottonseed, linseed, soybean, peanut), proteins (egg white, lean meat, hair), and esters (compounds that give fragrance to fruits and flowers).

All living (organic) material is made up of carbon compounds. Thus the vegetable materials that make up trees and plants are largely carbohydrates with some protein and other carbon compounds. In the course of the geologic changes that have taken place on the earth's surface, dense growths of trees, giant ferns, and other plants have become covered with water, soil, and rocks. As a result of the combined effect of pressure, heat, and bacterial action, this vegetable material has been destructively decomposed (carbonized) and has thereby been converted into coal. In certain localities the pressures and temperatures at which the carbonization occurred were such that a crystalline form of carbon known as *diamond* was formed. Peat, lignite, soft coal, hard coal, and graphite represent increasing degrees of carbonization of the submerged deposits of vegetable material.

The formation of charcoal (carbon) when wood, straw, coconut shells, corn cobs, and other vegetable materials are destructively distilled (see 18.8–2), and of coke when soft coal is decomposed, simulates certain aspects of what took place in nature during the formation of coal, graphite, and diamond.

21.3 Physical properties of carbon (see Table 21.1). Carbon exists in two crystalline allotropic forms, represented by diamond and graphite (see Figures 21.1 and 21.2) and one amorphous form represented by the carbon in coal, coke, and charcoal. Diamond is the hardest substance known; it owes this property to its characteristic crystal structure.

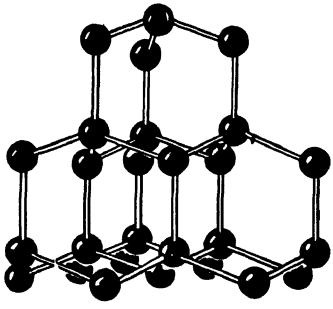


Figure 21.1. Crystal structure of diamond. The white lines represent the valence bonds holding the atoms of carbon (black spheres) together.

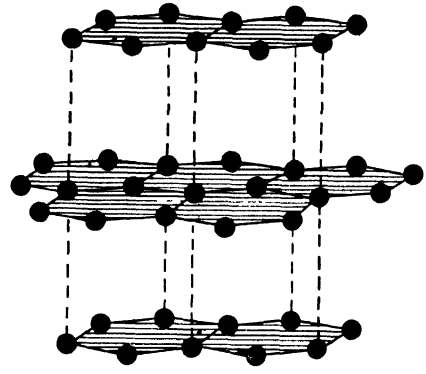


Figure 21.2. Crystal structure of graphite. The layers of carbon atoms are bound together by relatively weak valence bonds (dashed lines) and are therefore free to slip over each other.

In contrast, graphite is soft and greasy to the touch; it owes this property to the fact that the atoms in its crystals are arranged in layers, and these layers or planes are relatively free to slip over each other. When any form of carbon is vaporized (at 3500°C) graphite is formed when the vapor condenses.

Diamond and graphite have densities of 3.51 and 2.25, respectively. Amorphous carbon is microcrystalline in character. The extremely small size of the individual crystalline units gives it a porous character with a very large amount of surface per unit of mass. As a result, such forms as charcoal and coke have the ability to *adsorb* (attach to their surface) large quantities of gases and dissolved or dispersed material. This is the basis for the use of charcoal in gas masks and for removal of colored or odoriferous materials from various industrial solutions by running them through charcoal filters.

Lampblack, formed by incomplete combustion of methane and other hydrocarbon gases ($CH_4 + O_2 = C + 2\,H_2O$), is an extremely finely divided form of amorphous carbon which has many industrial uses.

Because crystal-clear diamonds are scarce, and because their high

refractive index and characteristic crystal structure cause them to sparkle with a striking and pleasing brilliance when properly cut, they are highly prized as precious stones. Because of their hardness, the imperfect and discolored specimens (black diamonds) are used in making tools for cutting and grinding steels and other hard alloys.

21.4 Chemical properties of carbon

1. The oustanding chemical property of carbon is its unique ability to share electrons with itself, forming thereby compounds containing long chains of carbon atoms. As a result there are thousands of different carbon compounds. This ability of carbon atoms to combine with each other is doubtless associated with the fact that they have a small atomic diameter and a symmetrical arrangement of four electrons in their valence shell. The long-chain carbon compounds will be discussed in Chapter 22. Only the oxygen compounds and their simple derivatives will be considered in this chapter.

2. It burns in air or oxygen to form CO_2.

3. It is a powerful reducing agent at high temperatures. It will reduce:

(a) *Metal oxides.* The products are free metal and either CO or CO_2.

$$2\,CuO + C\ (\text{heated}) = 2\,Cu + CO_2$$
$$ZnO + C\ (\text{heated}) = Zn + CO$$

The oxides of all metals below Al in oxidation potential can be reduced to the free metal by heating with carbon. The more reactive the metal, the higher the temperature required to accomplish the reduction. As the reduction temperature increases, the per cent of CO_2 formed as a product decreases and the per cent of CO increases. The reducing property of carbon is the basis for the wide use of coke and charcoal in the metallurgy of metals (see 25.11).

When an attempt is made to reduce the oxides of very reactive metals, such as aluminum or calcium, the carbide of the metal is formed.

$$2\,Al_2O_3 + 9\,C = 6\,CO + Al_4C_3$$
$$CaO + 3\,C = CaC_2 + CO$$

It is probable that free metal is first formed, but it reacts at once with carbon to form the carbide. Calcium carbide (CaC_2), prepared in this way, is a very important industrial compound.

(b) *Nonmetal oxides.* The products are the nonmetal and either CO or CO_2.

$$SiO_2 + 2\,C\ (2000°) = Si + 2\,CO$$
$$CO_2 + C\ (\text{heated}) = 2\,CO$$

This is the basis for the use of coke in the commercial preparation of silicon and phosphorus.

(c) *Steam*

$$C + H_2O \text{ (steam, heated)} = CO + H_2$$

This is the *water gas reaction* which takes place in the manufacture of one form of industrial fuel gas. Air and steam are alternately passed through a deep bed of coal or coke. The blast of air causes the exothermic reaction $C + O_2 = CO_2$ to take place; this causes the entire coal bed to become red hot. The air is then shut off and a blast of steam is blown in; the endothermic reaction given above then takes place, yielding the combustible gases CO and H_2.

In the presence of a catalyst the reaction is

$$C + 2\,H_2O \text{ (steam, heated)} = CO_2 + 2\,H_2$$

The CO_2 is dissolved in water or some alkaline solution, and hydrogen gas is recovered as a product. This is one important commercial source of hydrogen.

(d) *A number of different oxidizing compounds*, such as HNO_3, H_2SO_4, $KClO_3$, KNO_3, and Na_2O_2. High temperatures are required.

$$C + 4\,HNO_3 \text{ (conc, hot)} = CO_2 + 4\,NO_2 + 2\,H_2O$$
$$2\,KClO_3 + 3\,C \text{ (heated)} = 2\,KCl + 3\,CO_2$$

21.5 Commercial uses of carbon

1. Coal, coke, and charcoal are used as fuels.

2. Coke and charcoal are used in preparation of metals and nonmetals from their ores.

3. Coal, coke, and charcoal are used for manufacture of hydrogen, water gas, calcium carbide (CaC_2), and hundreds of different organic compounds.

4. Charcoal from wood, bones, and coconuts is used for adsorption of gases and for removal of undesirable colors from industrial solutions. Sugar solutions, for example, are often clarified by running them through charcoal filters.

5. Lampblack is used in the manufacture of rubber (tires, tubes, and sheets), ink, and paint.

6. Diamonds are used as precious stones and for making drill points and cutting tools.

Some idea of the industrial importance of carbon can be gathered from the fact that in 1950 the United States produced:

(a) 512,000,000 tons of soft (bituminous and lignite) coal

(b) 44,077,000 tons of hard (anthracite) coal

(c) 72,718,000 tons of coke

(d) 740,000,000 gallons of coal tar (by-product in manufacture of coke)

(e) 261,000,000 gallons of coal oil (by-product in manufacture of coke)

(f) 925,000 tons of ammonium sulfate (by-product in manufacture of coke)

(g) About 1 trillion cubic feet of coal gas (by-product in manufacture of coke)

(h) 691,000 tons of lampblack

21.6 Laboratory preparation of carbon monoxide. It is prepared by the dehydration of formic or oxalic acid.

$$\text{HCOOH (formic acid)} + H_2SO_4 \text{ (conc)} = H_2SO_4 \cdot X\,H_2O + CO\uparrow$$

$$(COOH)_2 \text{ (oxalic acid)} + H_2SO_4 \text{ (conc)} = H_2SO_4 \cdot X\,H_2O + CO\uparrow + CO_2\uparrow$$

When oxalic acid is used the CO_2 gas is absorbed by passing the mixture of gases through a solution of a strong base.

$$CO_2 + 2\,OH^- = CO_3^{--} + H_2O$$

The CO can be collected by displacement of water. It is a colorless, odorless, and *extremely poisonous* gas. It can be identified by the fact that, when burned in air, it yields CO_2 as the only product. The CO_2 that is formed can be detected by bringing it in contact with a solution of $Ca(OH)_2$ or $Ba(OH)_2$, with which it reacts to form a white precipitate ($CaCO_3$ or $BaCO_3$).

21.7 Commercial preparation of carbon monoxide by passing CO_2 gas over hot coke.

$$CO_2 + C \text{ (heated)} = 2\,CO$$

21.8 Chemical properties of carbon monoxide

1. It burns in air.

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

2. It is a strong reducing agent when heated.

$$Fe_2O_3 + 3\,CO = 2\,Fe + 3\,CO_2$$

21.9 Commercial uses of carbon monoxide

1. Synthesis of methyl alcohol (methanol)

$$CO + 2\,H_2 \text{ (heated, in presence of a catalyst)} = CH_3OH$$

Methyl alcohol has a large number of industrial uses, making this a very important synthesis. The CO for use in this process can be prepared by the water gas reaction:

$$C + H_2O = CO + H_2$$

2. Recovery of nickel from its ores. This use depends upon the fact that CO combines with nickel to form a volatile compound, nickel carbonyl, $Ni(CO)_4$.

$$Ni + 4\,CO = Ni(CO)_4$$

At higher temperatures the $Ni(CO)_4$ decomposes to form metallic nickel and CO.

21.10 The toxicity of carbon monoxide. As already noted, carbon monoxide is very poisonous. The fact that it is colorless and odorless makes it extremely treacherous. A headache may give warning of its presence, but too often this warning comes too late. It owes its toxic effect to the fact that it combines with the hemoglobin of the blood to form a stable compound. As a consequence the hemoglobin is unable to perform its vital role of carrying oxygen from the lungs to all parts of the body; lack of oxygen results in death. As little as 1 volume of CO in 500 volumes of air may be fatally toxic.

Carbon monoxide is always formed during the combustion process that takes place in an automobile engine, and is therefore present in the exhaust gases. This is because some carbon is always liberated when a gasoline-air mixture explodes (burns) in the cylinder of the engine. When this hot carbon comes in contact with CO_2 gas that is always formed when gasoline burns, CO is produced as an oxidation-reduction product ($C + CO_2 = 2\,CO$).

A less common but often more tragic source of CO is from stoves and furnaces in which faulty drafts do not allow entrance of enough air. The lower layers of coal in the furnace burn to yield CO_2 according to the reaction

$$C + O_2 = CO_2 + \text{heat}$$

The heat of this reaction raises the temperature of the overlying layers of coal to the point where some of the CO_2 that has been formed is reduced to CO.

$$CO_2 + C \text{ (heated)} = 2\,CO$$

When the drafts are open far enough to allow the entrance of enough air,

this CO burns with the characteristic blue flame that is noted on the surface of all coal fires (see Figure 21.3).

$$2\ CO + O_2 = 2\ CO_2 \text{ (blue flame)}$$

However, if the amount of entering air is limited, this CO will escape without being burned and may leak out through the walls of the upper part of the furnace or stove.

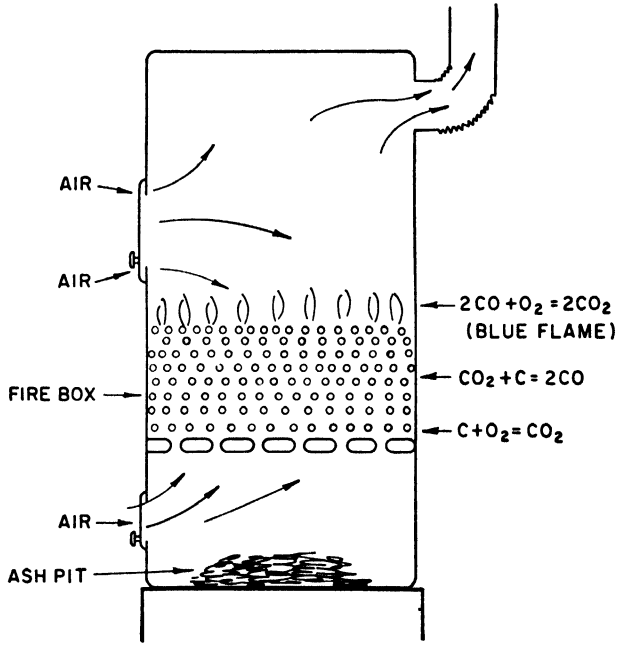


Figure 21.3. Reactions in a coal-burning stove.

Carbon monoxide is always formed when carbonaceous material (wood, oil, rags, paper, paint) burns in a limited supply of air. It is one of the most dangerous hazards that the fireman must face and is probably the immediate cause of many deaths in burning buildings.

21.11 Laboratory preparation of carbon dioxide

$$\text{Carbonate of a metal} + \text{a strong acid} = CO_2 + H_2O + \text{a salt}$$

$$CaCO_3 + 2\ H^+ = Ca^{++} + H_2O + CO_2\uparrow$$

Because the CO_2 is sparingly soluble it can be collected by displacement of water. It is a colorless gas which can be detected by the fact that it

extinguishes a lighted splint and gives a white precipitate ($CaCO_3$ or $BaCO_3$) when brought in contact with a solution of $Ca(OH)_2$ or $Ba(OH)_2$.

$$CO_2 + Ca^{++} + 2\,OH^- = \mathbf{CaCO_3}\text{ (white)} + H_2O$$

The fact that CO_2 gas does not support combustion and will therefore extinguish a flame is the basis for its use as a fire extinguisher.

Its preparation illustrates a typical salt + acid = new salt + new acid reaction. The acid, H_2CO_3, that is formed is unstable as well as being a weak electrolyte, and decomposes to give H_2O and the anhydride, CO_2 gas.

21.12 Other sources of carbon dioxide

1. Burning carbon or carbon compounds

$$C + O_2 = CO_2$$

$$C_6H_{10}O_5\text{ (wood)} + 6\,O_2 = 6\,CO_2 + 5\,H_2O$$

2. Reduction of less stable oxides by carbon

$$2\,CuO + C\text{ (heated)} = 2\,Cu + CO_2$$

3. Reduction of oxides by CO

$$PbO + CO\text{ (heated)} = Pb + CO_2$$

4. Catalytic reduction of steam by carbon

$$C + 2\,H_2O\text{ (heat; catalyst)} = CO_2 + 2\,H_2$$

This is a commercial method for preparing hydrogen.

5. Heating carbonates of less reactive metals

$$CaCO_3\text{ (heated)} = CaO + CO_2$$

The carbonates of all except the group IA metals will decompose in this fashion.

6. Heating the hydrogen carbonates (acid carbonates) of all metals

$$2\,NaHCO_3\text{ (heated)} = Na_2CO_3 + H_2O + CO_2$$

7. Oxidation of foods in the body

$$C_{12}H_{22}O_{11}\text{ (sugar)} + 12\,O_2 = 11\,H_2O + 12\,CO_2 + \text{heat}$$

This accounts for the presence of CO_2 in the gas that is exhaled from the lungs. The oxidation of the foods that are consumed supplies the heat and energy necessary to maintain the temperature and activity of the body and allow it to do work.

8. Numerous fermentation and bacterial processes

$$C_6H_{12}O_6 \text{ (glucose)} + \text{yeast} = 2\,C_2H_5OH + 2\,CO_2$$

This is the reaction that takes place in the commercial preparation of ethyl alcohol (C_2H_5OH) by fermentation of glucose ($C_6H_{12}O_6$).

21.13 Commercial sources of carbon dioxide

1. Combustion of coal or coke

$$C + O_2 = CO_2$$

The CO_2 gas is absorbed in a solution of Na_2CO_3, with which it reacts to form a precipitate of $NaHCO_3$.

$$CO_2 + 2\,Na^+ + CO_3^{--} + H_2O = 2\,\mathbf{NaHCO_3}$$

The solid $NaHCO_3$ is then heated to give CO_2, and the cycle is repeated.

$$2\,NaHCO_3 \text{ (heated)} = Na_2CO_3 + H_2O + CO_2$$

2. Catalytic oxidation of coke by steam (see 21.12)
3. Thermal decomposition of limestone to form quicklime

$$CaCO_3 \text{ (limestone, heated)} = CaO \text{ (quicklime)} + CO_2\uparrow$$

21.14 Physical properties of carbon dioxide. It is a practically odorless gas, but gives a choking sensation when inhaled. It has a density of 44 g/22.4 l at STP, being therefore somewhat heavier than air. It can be liquefied by a pressure of 56.3 atm at 20°C. Solid CO_2, known as *dry ice*, sublimes at −78.5°C.

21.15 Chemical properties of CO_2 and carbonic acid

1. CO_2 is the acid anhydride of the weak, unstable acid H_2CO_3.

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ + HCO_3^- \rightleftarrows H^+ + CO_3^{--}$$

2. At high temperatures CO_2 is reduced by carbon and active metals.

$$CO_2 + C \text{ (heated)} = 2\,CO$$
$$CO_2 + Mg \text{ (heated)} = MgO + CO$$

The latter reaction shows why CO_2 is not effective in extinguishing active-metal (Mg, Ca, Na, K) fires.

3. In the presence of plant chlorophyll as a catalyst and with sunlight providing the necessary energy, it reacts with moisture in the plant to produce starch and oxygen. The process is called *photosynthesis*. The

reaction, which is not well understood, may be represented by the equation

$$6\,CO_2 + 5\,H_2O = C_6H_{10}O_5 + 6\,O_2$$

This reaction is part of a *carbon cycle* by which carbon appears first as carbohydrate and other organic compounds in the structure of plants and animals, then as CO_2 in the air when these materials are oxidized or burned, then back to these compounds again by way of photosynthesis, and so on (see Figure 21.4). As a result of the removal of CO_2 from the air by photosynthesis and by dissolving in rain, the balance of CO_2 in nature is maintained.

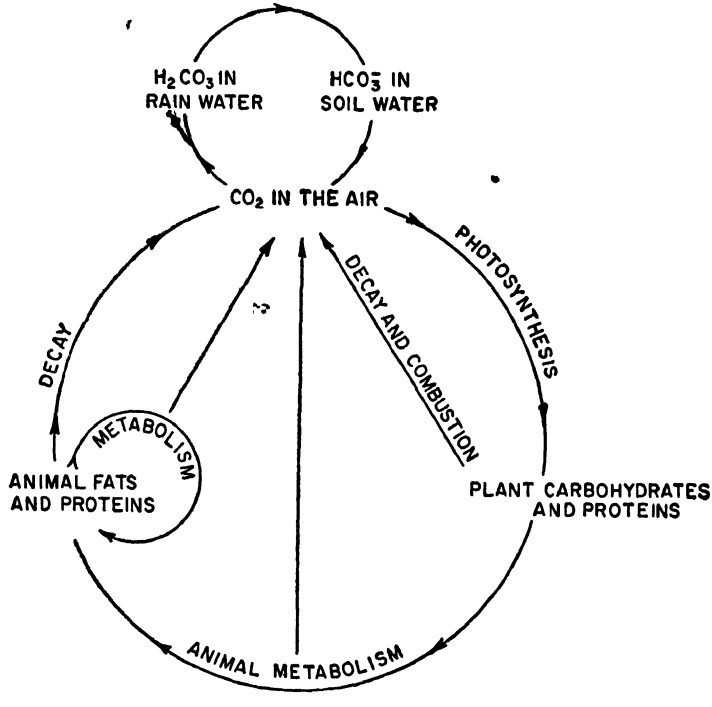


Figure 21.4. The carbon cycle.

4. Carbon dioxide and H_2CO_3 react with solutions of bases to form the carbonates of metals. All metal carbonates except those of ammonium and the metals of group IA are insoluble in water. All metal carbonates are soluble in strong acids.

21.16 Hydrolysis of carbonates and acid carbonates. The soluble metal carbonates (Na_2CO_3, K_2CO_3), being derived from bases that

are stronger electrolytes than the weak acid H_2CO_3, show an alkaline reaction when dissolved in water. The hydrolysis reaction is

(1) $$CO_3^{--} + H_2O \rightleftarrows HCO_3^- + OH^-$$

When an acid carbonate ($NaHCO_3$ or $KHCO_3$) is dissolved in water, the HCO_3^- ion will ionized as well as hydrolyze.

(2) $$HCO_3^- + H_2O \rightleftarrows H_2CO_3 + OH^-$$

(3) $$HCO_3^- \rightleftarrows CO_3^{--} + H^+$$

The fact that solutions of acid carbonates show an alkaline reaction shows that reaction (2) predominates over reaction (3).

Since the OH^- ion in equation (2) will combine with the H^+ ion in equation (3) to form H_2O, the over-all reaction for what happens when an acid carbonate is dissolved in water can be represented by the net equation

(4) $$2\,HCO_3^- \rightleftarrows H_2CO_3 + CO_3^{--}$$

The equilibrium represented by equation (4) accounts for the following experimental facts.

1. *That carbonates are converted to acid carbonates by treatment of the solution with excess* CO_2. The CO_2 reacts with water to form H_2CO_3. This H_2CO_3 shifts the equilibrium in equation (4) to the left, thereby converting the CO_3^{--} to HCO_3^- (see 21.13–1).

2. *The dissolving of a precipitate of* $CaCO_3$ *by excess* CO_2. When CO_2 is added to a solution of $Ca(OH)_2$, $CaCO_3$ is first precipitated. Addition of excess CO_2 causes the precipitate to redissolve. The solid $CaCO_3$, like all solid electrolytes, is in equilibrium with its ions.

(5) $$CaCO_3 \rightleftarrows Ca^{++} + CO_3^{--}$$

Excess CO_2 reacts with water to form H_2CO_3. This H_2CO_3 reacts with the CO_3^{--} ions in equation (5) to form HCO_3^- ions as in equation (4). Removal of CO_3^{--} causes the equilibrium in equation (5) to be shifted to the right; eventually the $CaCO_3$ will all be dissolved. This is the sort of reaction that takes place when limestone rocks are eroded as a result of contact with ground water which is laden with H_2CO_3. This erosion process has a number of interesting consequences:

(a) The ground water (spring and well water) acquires *temporary hardness* because of presence of Ca^{++} and HCO_3^- ions (see 13.15–3). When this water is boiled, in a teakettle for example, a white precipitate of $CaCO_3$, commonly called "lime," is deposited. The reactions that take place are discussed in 3 below.

(b) Limestone caves may be formed. Large fissures and caverns in underground limestone deposits are first formed as a result of contraction and fracture of the earth's outer crust. Carbonic-acid-laden water flows into these fissures, stands in contact with the limestone rock, and in the course of hundreds of years, gradually dissolves the limestone ($CaCO_3$) and produces caves such as Mammoth Cave.

(c) Stalactites and stalagmites are formed on the ceilings and floors, respectively, of limestone caves. As the H_2CO_3-laden ground water trickles down through the cracks in the limestone rock that constitute the roof and ceiling of a cave, it erodes the rock and thereby acquires increasing concentrations of Ca^{++} and HCO_3^- ions. As it slowly seeps through faults in the limestone ceiling and emerges into the air of the cave, evaporation of the water begins to take place. This results in precipitation of $CaCO_3$ in accordance with equation (5). Other dissolved minerals will also be precipitated along with the $CaCO_3$. At first the deposit is a tiny speck; as more exuding solution evaporates on the surface of the speck it grows in size; soon it is a "button," then a large knob, then a small "icicle," finally a good-sized stalactite. In the meanwhile some of the drops of the exuded solution have fallen to the floor of the cave, where some evaporation takes place and a speck of solid forms. As more drops fall and evaporate, the deposit increases in height and width, gradually becoming a columnar stalagmite of increasing size. Eventually the stalactite growing down from the ceiling may meet the stalagmite growing up from the floor, and a continuous column will then be formed. In similar fashion the evaporation of the water that exudes from cracks in the walls of the caves may produce all sorts of convolutions and figures. If the evaporating solution contains also colored salts of iron and other metals, deposits of varied and striking colors will be formed.

3. *Conversion of acid carbonates to normal carbonates by heating the solution.* Heat causes the H_2CO_3 in equation (4) to decompose, CO_2 gas being given off. Removal of the H_2CO_3 causes the equilibrium to shift to the right; this means that HCO_3^- ions will be converted to CO_3^{--} ions. For this reason a residue of Na_2CO_3 remains when a solution of $NaHCO_3$ is evaporated to dryness. The conversion of HCO_3^- to CO_3^{--} accounts for formation of a precipitate of $CaCO_3$ when a solution containing Ca^{++} and HCO_3^- ions is boiled. The increase in concentration of CO_3^{--} ions by boiling causes the equilibrium in reaction (5) to be shifted to the left. As a result, $CaCO_3$ is precipitated. This is exactly what happens when water that is temporarily hard because of presence of Ca^{++} and HCO_3^- ions yields a precipitate of $CaCO_3$ when boiled (see 13.15–3).

4. *Formation of a precipitate of* $CaCO_3$ *when a solution containing*

Ca^{++} *and* HCO_3^- *is treated with a base.* The base reacts with the acid (H_2CO_3) in equation (4). This shifts the equilibrium to the right, thereby increasing the concentration of CO_3^{--} ions. The increase in CO_3^{--} ion concentration causes the equilibrium in equation (5) to be shifted to the left; as a result $CaCO_3$ is precipitated.

21.17 Uses of carbon dioxide. The most important uses are: dry ice, for refrigeration; liquid CO_2 for fire extinguishers; preparation of carbonated drinks; manufacture of baking soda ($NaHCO_3$) and washing soda (Na_2CO_3) (see 35.5). Carbonated drinks owe their tang to the slight

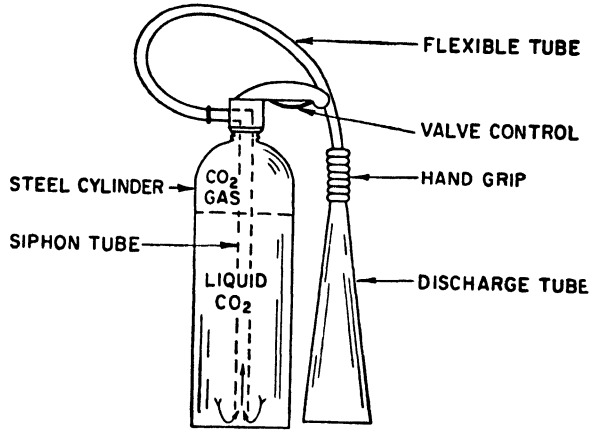


Figure 21.5. Carbon dioxide fire extinguisher.

acidity of the H_2CO_3 which they contain; they effervesce because of the escape from solution of the dissolved CO_2 gas when the pressure is reduced or the temperature is increased (see 11.5).

Questions

1. Give the evidence in support of the contention that, in group IVA, as the atomic number increases, the element becomes less nonmetallic and more metallic.

2. Account for the strongly nonpolar character of CH_4.

3. Sketch the carbon atom, showing the arrangement of all component parts. Sketch the following covalent molecules, showing in each case the character of the valence bonds: CCl_4, CS_2, CH_4, CO_2, CO, C_2H_6, H_2CO_3.

4. List the important chemical properties of carbon and give net equations to illustrate each.

5. List the important commercial uses of carbon, indicate in what form the carbon is used, and note the property upon which the use is based.

6. List the important chemical properties of CO and CO_2 and give net equations to illustrate each property.

7. How are CO_2 and CO produced commercially?

8. How would you distinguish between each of the following gases: H_2, CO, CO_2, SO_2, HCl, NH_3, and CH_4?

9. Indicate all ways in which CO_2 may be formed. Indicate also how the CO_2 that gets into the air is removed from the atmosphere. Write equations for all reactions.

10. How would you prove that C is a nonmetal?

11. Given coke as the only source of carbon, and any other substances and equipment that you need, show by a series of balanced chemical equations how each of the following can be prepared: CO_2, CO, Na_2CO_3, $NaHCO_3$.

12. When CO_2 is bubbled into a solution of lime water a white precipitate first forms; further addition of CO_2 causes this precipitate to disappear, a water-clear solution being formed. When a sample of this water-clear solution is boiled, a white precipitate is formed; likewise, a white precipitate is formed when the water-clear solution is treated with either NaOH or Na_2CO_3. Explain each of the above observations, giving net equations for all reactions.

13. When a sample of spring water was boiled, a white precipitate of $CaCO_3$ formed. How did the calcium carbonate get into the spring water?

14. List the important commercial uses of CO_2.

15. Solutions of the normal salt Na_2CO_3 and the acid salt $NaHCO_3$ both react alkaline to litmus paper. Explain.

16. A mixture of solutions of Na_2CO_3 and $Al_2(SO_4)_3$ is used as a fire extinguisher. Explain.

17. How would you identify each of the following solid substances: Na_2CO_3, $NaHCO_3$, NaCl, $NaClO_3$, NH_4Cl, Na_2SO_3, Na_2S, Na_2SO_4, NaBr, and P_4O_{10}?

18. What is photosynthesis? Discuss its role in nature.

19. Discuss all the possible chemical reactions that may take place in a coal-burning stove.

20. Account for the presence of carbon monoxide in automobile exhaust gas.

21. How many liters of dry CO_2 will be formed by complete combustion of 160 l of C_2H_2 gas, the volumes being measured at 40°C and 750 mm?

22. How many milliliters of 0.20 *M* HCl will be required to react with a solution containing 24 g of dissolved Na_2CO_3?

CHAPTER 22

Introduction to Organic Chemistry

22.1 Organic chemistry. The unique ability of carbon atoms to share electrons with each other and thereby form thousands of different compounds has been noted in Chapter 21. The study of these compounds, their preparation, properties, and uses is called *organic chemistry*. There are more than 480,000 organic compounds; a discussion of all of them would obviously be a very long story.

It will be the object of this chapter to give a brief introduction to organic chemistry by calling attention to certain characteristics of the compounds with which it deals, and pointing out the manner in which these compounds may be classified

22.2 General characteristics of organic compounds. An examination of all organic compounds shows that:

1. As a general rule they are covalent compounds. This follows from the fact that they are all derived from the hydrides of carbon, and these hydrides are covalent.

2. The majority are liquids or low-melting solids; many of the low-molecular-weight compounds are gases. This property is in line with the fact that they are covalent, since, as was pointed out in Chapter 7, covalent compounds generally have low melting points and boiling points.

3. The majority will burn in air. All contain carbon, nearly all contain hydrogen, and a large per cent contain oxygen. It is not surprising, therefore, to find that they are combustile; CO_2 and H_2O are generally formed as products.

4. The majority are insoluble in the polar solvent water but are soluble in nonpolar solvents such as benzene and heptane. These properties also are in line with their covalent and nonpolar character.

22.3 Broad classification of organic compounds. All organic compounds fall in one of two broad classifications:

1. *Hydrocarbons.* These compounds contain only hydrogen and carbon.

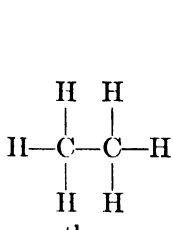
2. *Derivatives of hydrocarbons.* These compounds may all be looked upon, structurally, as hydrocarbons in which one or more hydrogen atoms have been replaced by other elements or groups of elements. The replacing element or group gives the derivative unique character and properties and is therefore referred to as a *functional group.* In the summary below, the functional group is given in boldface type.

Hydrocarbon	*Derivatives*
CH_4	$\mathbf{CH_3Cl}$, $\mathbf{CH_3OH}$, $\mathbf{CH_3CN}$, $\mathbf{CH_3NH_2}$, $\mathbf{CH_3COOH}$
C_6H_6	$\mathbf{C_6H_5OH}$, $\mathbf{C_6H_5NH_2}$, $\mathbf{C_6H_5CHO}$, $\mathbf{C_6H_5NO_2}$
C_2H_6	$\mathbf{(C_2H_5)_2O}$, $\mathbf{C_2H_4Br_2}$, $\mathbf{C_2H_5SH}$, $\mathbf{(C_2H_5)_2CO}$

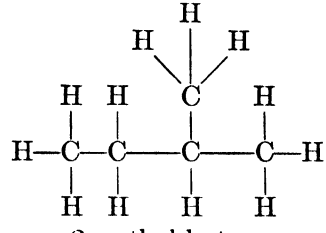
22.4 Classification of hydrocarbons; saturated and unsaturated. All hydrocarbons can be classified on the basis of whether or not there are any multiple bonds in their structure.

1. *Saturated hydrocarbons.* In these compounds every carbon atom is attached to every other carbon atom by a single valence bond (one pair of shared electrons).

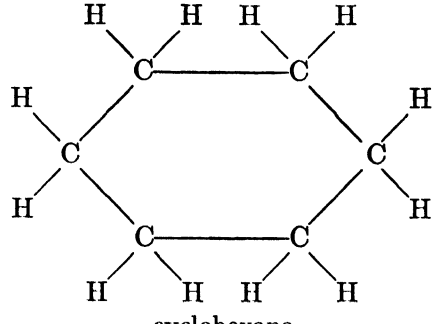
The following compounds are *saturated;* no more than one valence bond is used to attach any carbon atom to another carbon atom. (In all structures given in this chapter a single line represents a single covalent bond.) Each carbon atom employs 4 bonds.



ethane



2-methyl butane

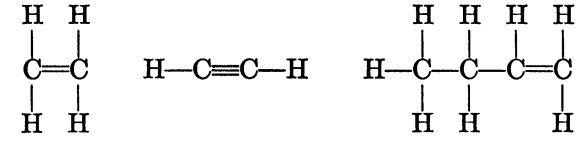


cyclohexane

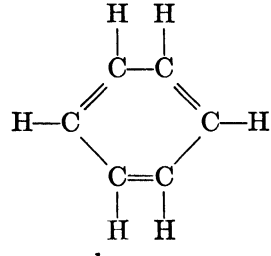
2. *Unsaturated hydrocarbons.* In these compounds one or more *pairs*

of carbon atoms are attached to each other by a double valence bond or a triple valence bond.

The following compounds are *unsaturated;* at least one pair of atoms in each molecule is bound together by a double or triple valence bond. Each carbon atom employs 4 bonds.



ethylene acetylene butylene



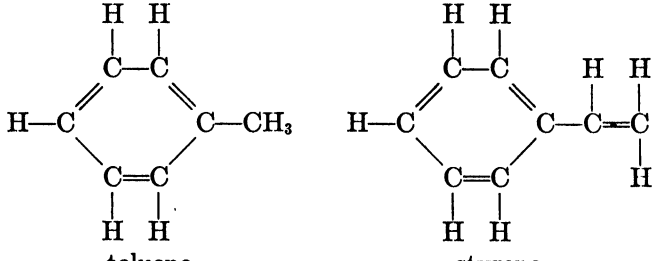
benzene

It is the general practice, when writing the nonstructural formulas for organic compounds, to show the location of all double and triple bonds. Thus the formula for butadiene is written $CH_2{=}CHCH{=}CH_2$, indicating that the first and second (from the left) and third and fourth carbon atoms are linked by double bonds, while the second and third are linked by a single bond. If one keeps in mind that each carbon atom must always employ 4 bonds, the double or triple bonds can be located if the formula is written in the form $CH_2CHCHCH_2$.

22.5 Classification of hydrocarbons; aromatic and aliphatic

1. *Aromatic hydrocarbons.* This includes benzene (see formula above), and all hydrocarbons that contain the benzene ring structure. Since benzene is an unsaturated hydrocarbon, all aromatic hydrocarbons are unsaturated.

The following hydrocarbons are *aromatic:*



toluene styrene

2. *Aliphatic hydrocarbons.* This includes those that are not aromatic. The aliphatic hydrocarbons may be either saturated or unsaturated. The large majority of aliphatics have a straight chain as a basic structure.

The following hydrocarbons are *aliphatic.*

C_4H_{10}	$CH_3CH{=}CH_2$	$CH_3CH_2H{\equiv}CH$	CH_4
butane	propylene	1-butyne	methane

22.6 Homologous series. Among all related hydrocarbons, whether they are aliphatic or aromatic, saturated or unsaturated, a compound containing 1 more carbon atom can be derived from a given hydrocarbon by adding 1 atom of carbon and 2 atoms of hydrogen. In this way is obtained an *homologous series of hydrocarbons*, that is, a series in which there is a constant difference of CH_2 between each member. Thus we have:

(a) CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, C_6H_{14}, C_7H_{16}, etc. These are the first 7 members of the *alkane* homologous series of saturated aliphatic hydrocarbons. The hydrocarbons of this series all have the general formula C_nH_{2n+2}.

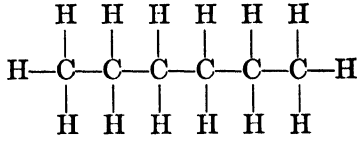
(b) $CH_2{=}CH_2$, $CH_3CH{=}CH_2$, $C_2H_5CH{=}CH_2$, $C_3H_7CH{=}CH_2$, $C_4H_9CH{=}CH_2$. These are the first 5 members of the *alkene* homologous series of unsaturated (double bond) aliphatic hydrocarbons. Their general formula is C_nH_{2n}.

(c) $CH{\equiv}CH$, $CH_3C{\equiv}CH$, $C_2H_5C{\equiv}CH$, $C_3H_7C{\equiv}CH$, $C_4H_9C{\equiv}CH$. These are the first 5 members of the *alkyne* homologous series of unsaturated (triple bond) aliphatic hydrocarbons. Their general formula is C_nH_{2n-2}.

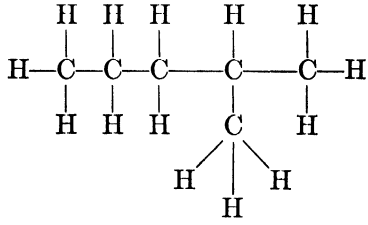
(d) C_6H_6, $C_6H_5CH_3$, $C_6H_5C_2H_5$, $C_6H_5C_3H_7$, $C_6H_5C_4H_9$. These are the first 5 members of the *benzene* homologous series of aromatic hydrocarbons. Their general formula is C_nH_{2n-6}.

22.7 Straight and branched aliphatic chains. Isomers. The carbon atoms in alkanes, alkenes, and alkynes may be linked together so as to form either a straight chain or a branched chain. Thus we may have the following five linkages in the alkane whose empirical formula is C_6H_{14}.

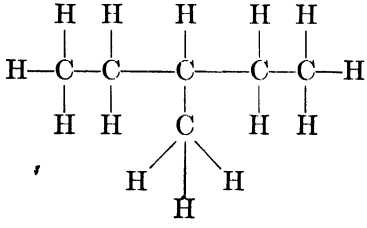
(1)



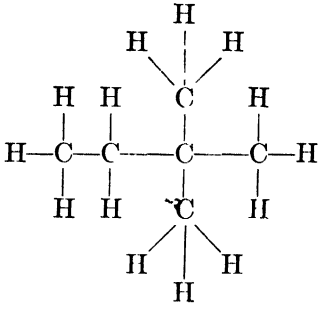
(2)



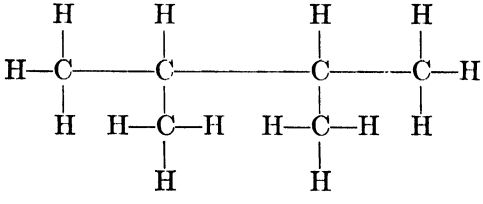
(3)



(4)



(5)



In these formulas, (1) is a *straight-chain* hydrocarbon; (2), (3), (4), and (5) are *branched-chain* hydrocarbons. The branches are referred to as *side chains*. Each of the 5 compounds has the same empirical formula, C_6H_{14}, but because of the difference in their structures, their boiling points and other properties are different. The 5 compounds are referred to as *isomers* because *they have the same empirical formulas and molecular weights but differ in structure.*

It should be noted that some aliphatic compounds have a ring structure (see cyclohexane, 22.4–2). All aromatics have the basic benzene ring structure; however, this benzene ring may, and very commonly

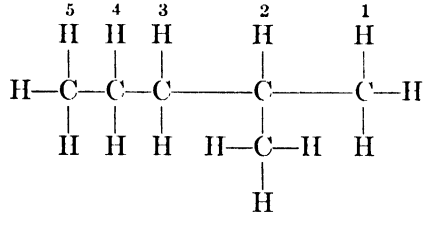
does, have a straight-chain aliphatic side chain (see styrene, 22.5).

22.8 Names of hydrocarbons. The name of a hydrocarbon should reveal its class and structure. Thus if it is classed as a saturated alk*ane* its name ends in *ane;* the first four members of the alkanes are meth*ane* (CH_4), eth*ane* (C_2H_6), prop*ane* (C_3H_8), and but*ane* (C_4H_{10}). Thereafter the prefix denotes the number of carbon atoms: pent*ane* (C_5H_{12}), hex*ane* (C_6H_{14}), dec*ane* ($C_{10}H_{22}$), etc.

If it is a branched-chain compound, the name must reveal the location of the side chain and must identify the side chain. Note that in formulas (2), (3), (4), and (5) in 22.7 the side chains are all CH_3 groups. The CH_3 group is the *methyl group;* note that its name is derived from the alkane (methane) by substituting *yl* for *ane.* By the same rule C_2H_5 is the *ethyl* group, C_3H_7 is *propyl* and so on, $C_{10}H_{21}$ being *decyl.* The C_6H_5 group is the *phenyl* group.

In naming a branched-chain saturated hydrocarbon, take the longest straight-chain unit, call that the basic chain, and number the carbon atoms in it consecutively from 1 up, *starting with the carbon at the end closest to the side chain.* Thus for the hydrocarbon

(2)

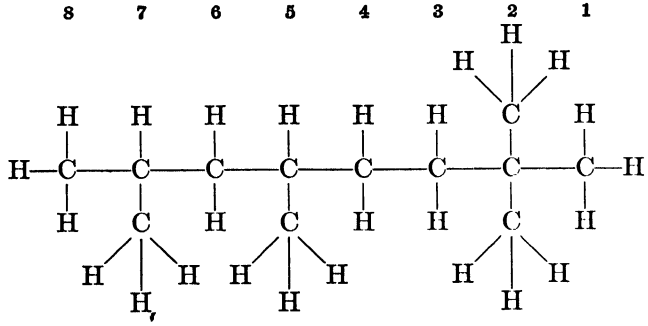


the longest straight chain is the horizontal one; this is a *pentane* (5-carbon alkane). The carbon atoms in this chain are numbered from the right end in the manner shown, since the side chain (CH_3) is closest to that end. Since the methyl group is attached to the second carbon atom of the pentane chain, the name will be *2-methyl pentane.* The compound represented by formula (3) of Section 22.7 is also a *pentane.* The methyl group is attached in the middle, so it can be numbered from either end. The name of the compound is *3-methyl pentane.* Compounds (4) and (5) are both *butanes* because the longest chain has 4 carbon atoms; (4) must be numbered from the right end, but (5) can be numbered from either end. Since there are two methyl side chains in each of these compounds they are both *dimethyl butanes.* Compound (4) is *2,2-dimethyl butane;* this indicates that both methyl groups are attached to the second carbon atom. Compound (5) is *2,3-dimethyl butane.*

If an alkane chain has several side chains attached to different carbon atoms, *the numbering should start from that end which is closest to the*

greater number of attached carbon atoms. Thus compound (6) is 2,2,5,7-tetramethyl octane.

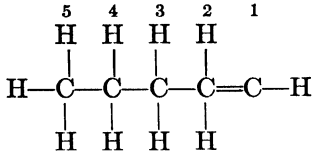
(6)



The name of an alkene and an alkyne must show the position of the double or triple bond as well as the positions of all side chains. First of all, the *chain containing the double or triple bond* is taken as the basic chain. *The carbon atoms are numbered, starting from the end closest to the double or triple bond;* this is done regardless of where the side chains are located. This is in accord with the general rule that the numbering of a chain starts at that end which is closest to the *identifying feature* of the compound. The position of the double or triple bond is identified by giving it the number of the *lowest-numbered carbon atom* to which it is attached.

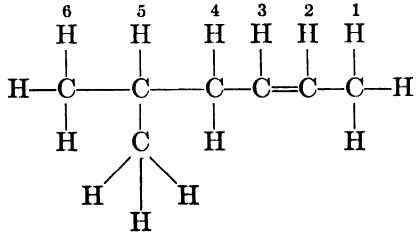
By the above rule compound (7) is *1-pentene:*

(7)



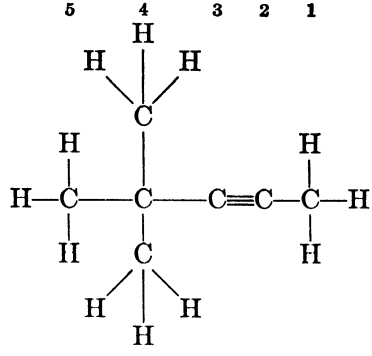
Compound (8) is *5-methyl-2-hexene:*

(8)



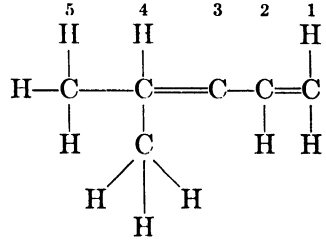
Compound (9) is *4,4-dimethyl-2-pentyne:*

(9)



Compound (10) is *3-methyl-1,3-pentadiene;* the ending, *diene,* shows that there are 2 double bonds.

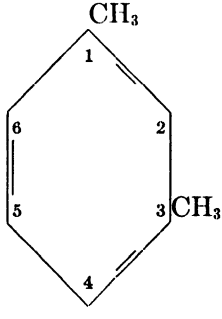
(10)



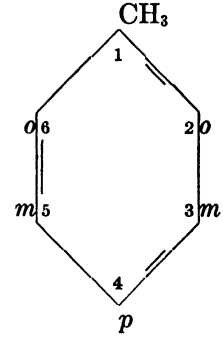
It should be noted that except for HC≡CH, which is called *acetylene,* the alkenes and alkynes are named by using the same prefixes as are used in naming the alkanes.

In naming a hydrocarbon of the benzene series (aromatic) the carbon atoms of the benzene ring are generally numbered in a clockwise manner, starting with 1 at the top. It is customary to use a simple hexagon to represent this ring. The structural formula and numbering will then be as noted in compound (11); the name of this compound is *1,3-dimethyl benzene,* while (12) is *methyl benzene.*

(11)

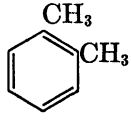


(12)

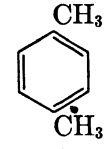


The common name of (11) is *xylene* and of (12) is *toluene.*

The positions of the carbon atoms are also designated by the terms *ortho* (*o*), *meta* (*m*), and *para* (*p*). That carbon atom in the ring which has attached to it the group or side chain with the identifying feature is selected as the reference atom. The carbon atom next to this atom, on either side is in the *ortho* position; the second atom away from the reference atom on either side is in the *meta* position; the atom opposite is in the *para* position. Thus in compound (12) atom 1, containing the methyl side chain, is the reference atom; atoms 2 and 6 are in the *ortho* positions, atoms 3 and 5 are in the *meta* positions, and atom 4 is in the *para* position. Compound (11) is *m*-xylene because the second methyl group is in the *meta* position with respect to the reference carbon atom to which the first methyl group is attached. Compound 13 is *o*-xylene, while (14) is *p*-xylene.

(13) 

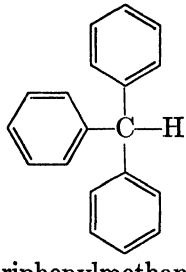
o-xylene

(14) 

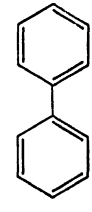
p-xylene

The number system is the simplest one, and is gradually replacing the *o-m-p* usages. However, the latter is still employed in naming so many compounds that familiarity with it is necessary for intelligent reading of organic chemical literature.

If the benzene ring is looked upon as a side chain it is called the *phenyl* group. Thus compound (15) is *triphenylmethane* and (16) is *diphenyl*.

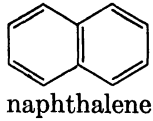
(15) 

triphenylmethane

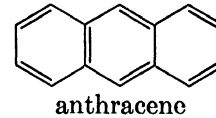
(16) 

diphenyl

Compound (17) is *naphthalene* (moth balls), and (18) is *anthracene*.

(17) 

naphthalene

(18) 

anthracene

22.9 Physical properties of the hydrocarbons

1. They are all insoluble in water but soluble in benzene. This is to be expected from the fact that they are all nonpolar compounds.

2. In any homologous series, as the molecular weight increases, the boiling point and melting point of the hydrocarbon increase. Those with fewer than 5 carbon atoms are gases. In the aliphatic series, those with more than 18 carbon atoms are, as a rule, waxlike solids, while those with from 5 to 18 carbon atoms are liquids. This regularity of boiling point increase is the basis for the separation of the components

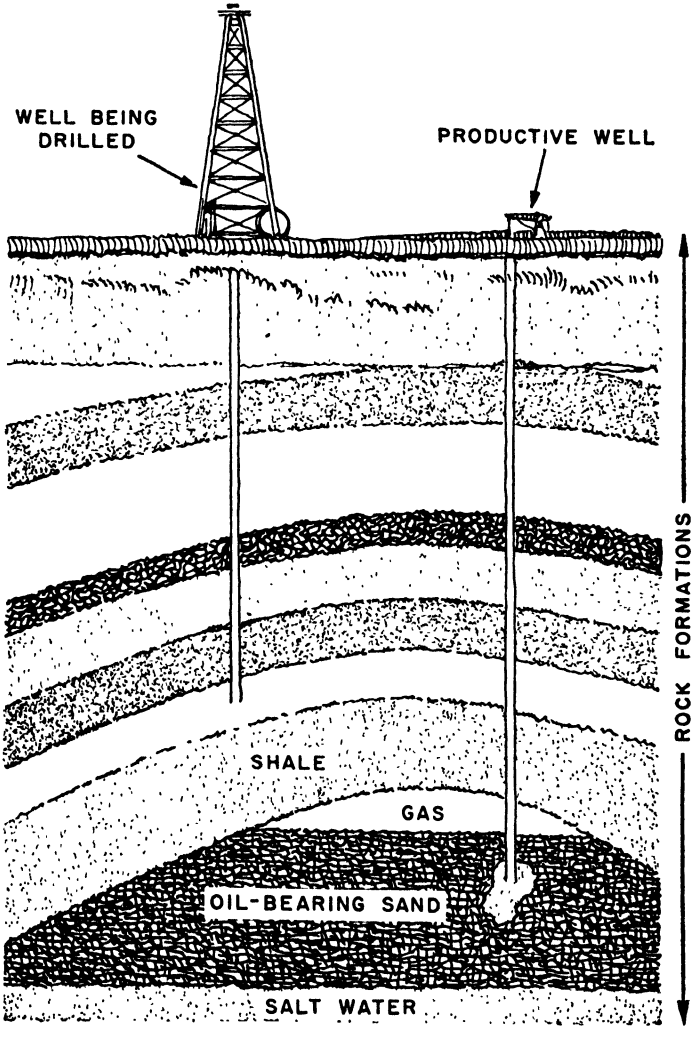


Figure 22.1. An oil well.

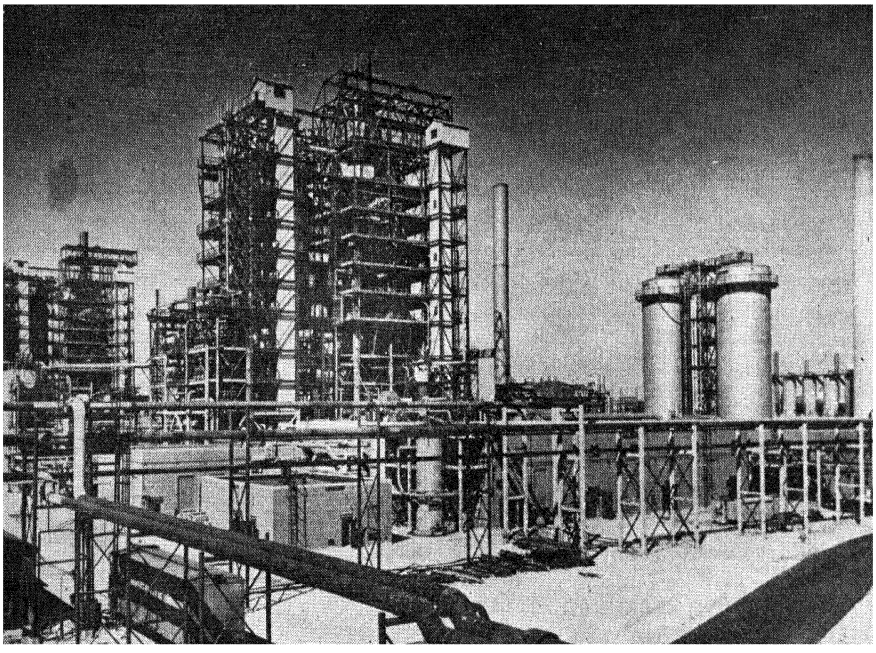


Figure 22.2. A battery of fluid catalytic cracking units in a modern oil refinery. Each unit processes about 1,200,000 gallons of petroleum per day and produces about 600,000 gallons of gasoline. Among the important by-products are unsaturated hydrocarbon gases which are used for the manufacture of plastics, synthetic rubber, alcohols and other products. (*Courtesy Standard Oil Company of Indiana*)

of natural petroleum, which is a mixture of alkanes, by *fractional distillation* (see 11.9-3). The lowest alkane, CH_4 (methane), is the chief component of natural gas. Ordinary straight-run gasoline obtained by fractionation of petroleum consists largely of the alkanes heptane, octane, nonane, and decane.

It is of interest to note that the United States produces annually about 6.3 trillion cubic feet of natural gas, 7.6 billion gallons of natural high-test gasoline and liquefied hydrocarbon gases, and 83 billion gallons of petroleum (see Figures 22.1, 22.2 and 22.3).

3. As a general rule, branched-chain isomers have lower boiling points, and hence are more volatile than the straight-chain compound. The greater the amount of branching, the lower the boiling point. Also, the greater the amount of branching the higher the *octane number* (the higher its antiknock property). This explains why, in the synthesis of modern gasolines, effort is made to get a high per cent of branched isomers.

22.10 Chemical properties of the saturated hydrocarbons

1. They are not particularly reactive.
2. They burn readily in air to form CO_2 and H_2O. This is the basis

for their use as fuel in internal combustion engines, oil burners, steam power plants, and the like.

3. They decompose at high temperatures and pressures to give hydrocarbons of lower molecular weight, carbon, and hydrogen; the mixture of hydrocarbons contains a high per cent of alkenes. This is the basis for the industrial *cracking* of high-molecular-weight petroleum components to give gasoline. It is also the basis for the manufacture of carbon black by thermal decomposition of methane and ethane.

4. They react with halogens to form substitution products.

$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl$$

This, we shall find, is an important step in the synthesis of organic compounds. The number of hydrogen atoms that are replaced will vary with the temperature and duration of the reaction.

5. They react with nitric acid to form nitro compounds.

$$C_2H_6 + HNO_3 = C_2H_5NO_2 + H_2O$$

22.11 Chemical properties of the unsaturated hydrocarbons

1. They are as a rule more reactive than the saturated hydrocarbons. This is due to the presence of the reactive double and triple bonds. Because of their reactivity they are of special importance in the synthesis of a variety of organic compounds.

2. They react by *addition* of substances to the double and triple bonds to form saturated compounds. They add:

Figure 22.3. One of the world's largest oil refineries, located at Whiting, Indiana. (*Courtesy Standard Oil Company of Indiana*)



(a) Hydrogen. This is called *hydrogenation.*

$$CH_2{=}CH_2 + H_2 = C_2H_6$$

(b) Halogens. This is called *halogenation.*

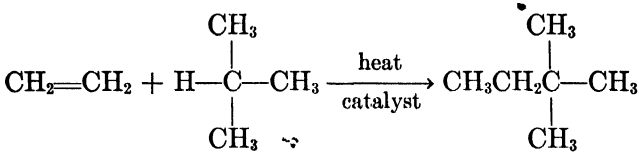
$$CH_2{=}CH_2 + Br_2 = BrCH_2CH_2Br$$

This illustrates the commercial method for preparing ethylene bromide. It is used in the manufacture of "ethyl" gasoline. So-called "ethyl" gas contains lead tetraethyl [$Pb(C_2H_5)_4$] as an antiknock component. When the $Pb(C_2H_5)_4$ burns in the cylinder, metallic lead is deposited. This lead fouls up the cylinders. The ethylene bromide prevents deposition of lead by converting it to volatile lead bromide.

(c) Acids

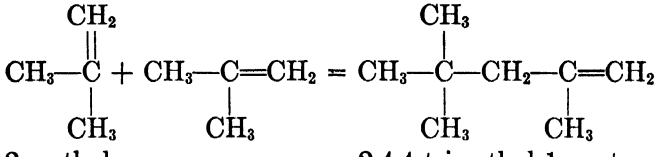
$$CH_2{=}CH_2 + HBr = CH_3CH_2Br$$

(d) Saturated hydrocarbons. This is called *alkylation.*



Alkylation is an important reaction in the synthesis of modern gasolines.

(e) By self-addition. Two or more molecules of the unsaturated hydrocarbon combine with each other to form a compound of higher molecular weight. This is called *polymerization,* and the product is a *polymer* of the original *monomer.*



2-methyl propene 2,4,4-trimethyl-1-pentene

This type of reaction is involved in the preparation of plastics and synthetic rubber. The polymers that are formed may contain up to 1500 or more units of the monomer. Their chainlike and weblike structures give the product its characteristic plastic quality. The capacity to form chain-type polymers is well illustrated by *isoprene.* The free bonds at the ends of the two interlinked isoprene units can link up with two more such units, and so on.

$$2\ CH_2{=}C(CH_3){-}CH{=}CH_2$$

isoprene
(2-methyl-1,3-butadiene)

$$= -CH_2-C(CH_3)=CH-CH_2\diagdown\!\diagup-CH_2-C(CH_3)=CH-CH_2-$$

two interlinked isoprene units

22.12 Preparation of some hydrocarbons

1. *Methane*, CH_4. It is prepared by the reaction of sodium acetate with soda lime (CaO + NaOH).

$$CH_3COONa + NaOH\ (\text{heated}) = CH_4\uparrow + Na_2CO_3$$

2. *Acetylene*, C_2H_2. It is prepared by the reaction of calcium carbide with water.

$$CaC_2 + 2\ H_2O = Ca(OH)_2 + C_2H_2\uparrow$$

This is a very important commercial reaction because the acetylene is used as a fuel, in oxyacetylene welding, and in the synthesis of a number of organic compounds. Manufacture of the synthetic rubber *neoprene* by polymerization of acetylene illustrates how an important industrial product can be prepared from the common raw materials limestone, coke, common salt, and water.

$$CaCO_3\ (\text{limestone})\ (\text{heated}) = CaO + CO_2$$

$$CaO + 3\ C\ (\text{coke})\ (\text{heated in electric furnace}) = CaC_2\ (\text{calcium carbide}) + CO$$

$$CaC_2 + 2\ H_2O\ (\text{steam}) = C_2H_2 + Ca(OH)_2$$

$$2\ NaCl\ (\text{common salt}) + 2\ H_2O\ (\text{electrolysis}) = 2\ NaOH + H_2 + Cl_2$$

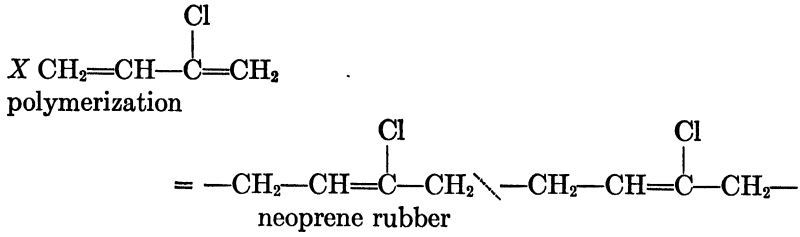
$$H_2 + Cl_2 = 2\ HCl$$

$$H{-}C{\equiv}C{-}H + H{-}C{\equiv}C{-}H \xrightarrow[\text{catalyst}]{\text{heat}} CH_2{=}CH{-}C{\equiv}CH$$

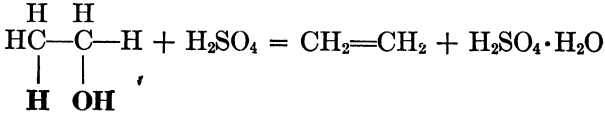
polymerization of acetylene — 3-butene-1-yne

$$CH_2{=}CH{-}C{\equiv}CH + HCl = CH_2{=}CH{-}C(Cl){=}CH_2$$

addition of HCl — 2-chloro-1,3-butadiene



3. *Ethylene*, C_2H_4. It is prepared by dehydration of ethyl alcohol (C_2H_5OH) with concentrated sulfuric acid, phosphoric acid, or alumina (Al_2O_3).

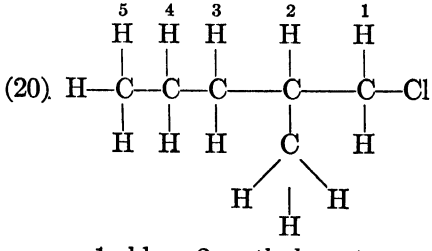


This is an important industrial reaction, the ethylene being used for preparation of a large number of organic compounds such as ethylene bromide (see 22.11) and various plastics.

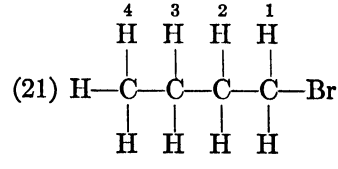
4. *Benzene, toluene, xylene, naphthalene*, and *anthracene* (see formulas 11, 12, 17, and 18) are formed in the destructive distillation of coal and are recovered from the coal tar.

22.13 Formation of derivatives of the hydrocarbons. Functional groups. The hydrocarbon derivatives may be looked upon, structurally, as having been formed from the hydrocarbon by replacement of one or more hydrogen atoms by one or more elements or radicals (groups). The actual preparation may be carried out by replacement (see 22.10), addition (see 22.11), or some more complex process. The replacing group gives the derivative unique characteristics and properties, and is therefore called a *functional group*.

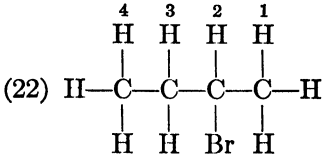
The compound is named, preferably, as a derivative of the hydrocarbon; or it may be identified by the functional group and named accordingly. In any case the longest chain containing the functional group is selected as the basic chain. The naming of the following derivatives will serve as illustrations.



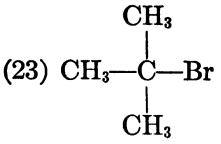
1-chloro-2-methyl pentane



1-bromobutane

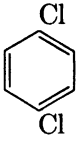
(22) 

2-bromobutane

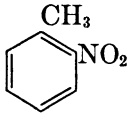
(23) 

1,1-dimethyl-1-bromoethane

Aromatic derivatives are named by numbering the carbon atoms or designating them as *m*, *o*, or *p* in the manner described in Section 22.8. The following compounds will serve as illustrations.

(24) 

1,4-dichlorobenzene
or *p*-dichlorobenzene

(25) 

1-methyl-2-nitrobenzene
or *o*-nitrotoluene

Some of the more important derivatives are discussed briefly in Sections 22.14 to 22.22.

22.14 Alkyl and aryl halides. They all contain halide (Cl, Br, I, or F) as the functional group. They have the general formula RX, in which R is any hydrocarbon group either aliphatic (*alkyl*) or aromatic (*aryl*), and X is either Cl, Br, I, or F. Some common halogen derivatives and their common uses are:

1. *Methyl chloride*, CH_3Cl. Refrigerant in refrigerators and deep-freeze units.
2. *Chloroform*, $CHCl_3$. Anesthetic in surgery.
3. *Carbon tetrachloride*, CCl_4. Solvent.
4. *Dichlorodifluoromethane* (Freon), CCl_2F_2. Refrigerant in refrigerators and deep-freeze units.
5. *p-dichlorobenzene*, $C_6H_4Cl_2$. Moth repellant; fumigant.
6. *Hexachlorocyclohexane*, $C_6H_6Cl_6$. Insecticide.
7. *DDT*, *dichlorodiphenyltrichloroethane*, $(C_6H_4Cl)_2CHCCl_3$. Insecticide.

22.15 Alcohols. They all contain —OH as the functional group and have the general formula ROH. Their names end in *ol*, signifying the presence of the OH group. They may contain one or more OH groups and are referred to, accordingly, as monohydric or polyhydric alcohols. Because of the presence of the polar OH group, the lower-molecular-

weight homologs are soluble in water. This property, plus the fact that they are nonelectrolytes and do not therefore exert any corrosive action on metals, is the basis for their use as antifreeze agents in automobiles. They react with acids to form esters (see 22.17), burn in air, and are readily oxidized.

They are named by replacing with *ol* the *e* in the name of the hydrocarbon from which they are derived. Thus C_2H_5OH is *ethanol* (from ethane). Dihydric alcohols are commonly referred to as *glycols*. Thus $HOCH_2—CH_2OH$ is called *ethylene glycol*, or *1,2-ethanediol*.

Some common alcohols and their important uses are:

1. *Methanol*, methyl alcohol, CH_3OH. Antifreeze, solvent, fuel, and reactant in the synthesis of other compounds (see 21.9).

2. *Ethanol*, ethyl alcohol, C_2H_5OH. It is formed by fermentation of sugars (see 21.12–8) and by synthesis from ethylene. It is widely used in the synthesis of organic compounds, as a solvent, as an antifreeze, and as an intoxicant.

3. *Phenol*, C_6H_5OH (carbolic acid). Antiseptic, manufacture of picric acid (2,4,6-trinitrophenol), and synthesis of other organic compounds.

4. *Ethylene glycol*, $C_2H_4(OH)_2$ (1,2-ethanediol). Antifreeze (*Prestone*, etc.).

5. *Glycerol*, $C_3H_5(OH)_3$ (glycerine). Manufacture of nitroglycerine (glyceryl trinitrate) and synthesis of organic compounds.

22.16 Acids. They all contain the $-\overset{\overset{O}{\|}}{C}-OH$ (carboxyl) functional group (commonly written —COOH) and have the general formula RCOOH. They may contain 1 or more —COOH groups and are accordingly referred to as mono-, di-, or tri-carboxylic acids. They are all weak acids. Those of high molecular weight (C_{15}) are insoluble oily liquids; because of this fact, the aliphatic acids are often referred to as *fatty acids*. The acids are named by replacing the *e* of the hydrocarbon of the same number of carbon atoms with the ending *oic*. Thus CH_3COOH is *ethanoic* acid, from *ethane* and $C_5H_{11}COOH$ is *hexanoic* acid, from *hexane*.

Some common acids and their occurrence are:

1. *Acetic* (ethanoic), CH_3COOH. It is the acid component of vinegar. It is formed when ethyl alcohol is oxidized

$$(C_2H_5OH + O_2 = CH_3COOH + H_2O).$$

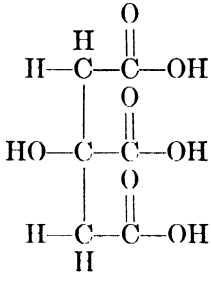
2. *Formic* (methanoic), HCOOH. It is the acid component that causes the pain resulting from insect bites and bee stings.

3. *Butyric* (butanoic) C_3H_7COOH. It gives the characteristic odor to rancid butter.

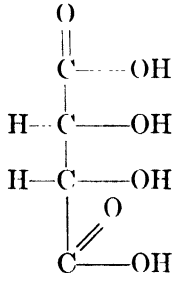
4. *Lactic* (hydroxypropanoic) $CH_3CHOHCOOH$. It is the acid component of sour milk.

5. *Oxalic* $(COOH)_2$. It is present in gooseberries, rhubarb, cranberries, and other tart fruits.

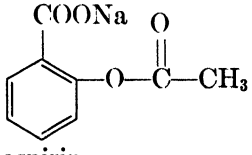
6. *Citric*. It is present in citrus fruits.



7. *Tartaric*. It is present in grapes and other fruits.



8. *Aspirin* is the sodium salt of acetyl salicylic acid. About 40 million aspirin tablets (about 15 tons) are consumed in the United States every day.



aspirin

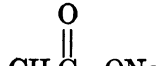
22.17 Acid anhydrides. They are related to organic acids just as the inorganic anhydrides SO_3 and N_2O_5 are related to the acids H_2SO_4 and HNO_3. When combined with water they form the acid. Their general formula is $(RCO)_2O$.

$$(CH_3CO)_2O + H_2O = 2\,CH_3COOH$$

acetic anhydride acetic acid

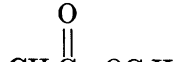
22.18 Esters. They contain alkyl or aryl radicals in combination with the anion of an acid. They contain an alkyl or aryl group in place of the metal normally present in the corresponding salt (RCOOR).

Salt



sodium acetate

Ester



ethyl acetate

They can be formed by the interaction of an acid and an alcohol.

$$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O$$

acid alcohol ester water

Most esters are volatile liquids. They generally have characteristic odors; specific esters are responsible for the tastes and odors of fruits and flowers. Some of these esters are given below.

Name of ester	*Formula*	*Odor*
isoamyl acetate	$CH_3COOC_5H_{11}$	banana
methyl butyrate	$C_3H_7COOCH_3$	pineapple
ethyl butyrate	$C_3H_7COOC_2H_5$	apricot, peach
isoamyl isovalerate	$C_4H_9COOC_5H_{11}$	apple
methyl salicylate	$C_6H_4OHCOOCH_3$	wintergreen

Fats and *oils* are glyceryl esters [derived from the alcohol, glycerine, $C_3H_5(OH)_3$] of the fatty acids.

glyceryl palmitate	$C_3H_5(C_{15}H_{31}COO)_3$
glyceryl oleate	$C_3H_5(C_{17}H_{33}COO)_3$
glyceryl stearate	$C_3H_5(C_{17}H_{35}COO)_3$

The oils listed above are present in cottonseed and olive oil as well as other vegetable oils.

Just as a salt will react with a base to form a new salt and a new base, so an ester will react with a base to form a salt and an alcohol. If the ester is a fat or oil (a glyceryl ester of a high fatty acid) the salt is a *soap*, the alcohol is glycerine, and the reaction process is known as *saponification.*

$$C_3H_5(C_{17}H_{35}COO)_3 + 3\,NaOH = C_3H_5(OH)_3 + 3\,C_{17}H_{35}COONa$$

glyceryl stearate glycerine soap (sodium stearate)

This illustrates a commercial method for preparing soap. *Detergents* such as *Dreft* are largely sodium lauryl sulfate, $CH_3(CH_2)_{10}CH_2SO_4Na$. *Nitroglycerine* is glyceryl trinitrate, $C_3H_5(NO_3)_3$.

22.19 Ethers. They are organic oxides and have the functional —C—O—C— linkage and the general formula R—O—R. They are generally quite volatile, inflammable, and nonreactive. They are excellent solvents for many organic substances. *Diethyl ether*, $(C_2H_5)_2O$, is the ordinary ether used as an anesthetic. Ethers can be prepared by dehydration of alcohols.

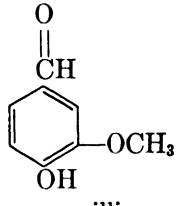
$$\underset{\text{alcohol}}{2\ C_2H_5OH} \xrightarrow[H_2SO_4]{-H_2O} \underset{\text{ether}}{(C_2H_5)_2O}$$

22.20 Aldehydes. Aldehydes have the functional group —C(=O)—H and the general formula RCHO. They are of great importance in the synthesis of a variety of organic compounds.

Formaldehyde, HCHO, is used for preserving biological specimens and as an embalming fluid, insecticide, and disinfectant. It is used in the synthesis of plastics, the best known one being *Bakelite*, which is formed by its reaction with phenol.

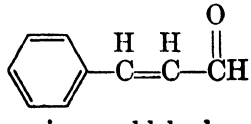
Benzaldehyde, C_6H_5CHO, gives the characteristic odor to almonds and almond oil.

Vanillin (vanilla) is 3-methoxy-4-hydroxybenzaldehyde.



vanillin

Cinnamaldehyde (cinnamon) is 3-phenyl-2-propene-1-al.



cinnamaldehyde

22.21 Ketones. Ketones have the functional *carbonyl* group =C=O and the general formula R_2 O. It should be noted that both aldehydes

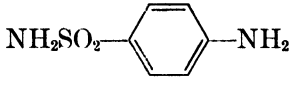
and ketones contain the carbonyl group. As a consequence they show a number of similar reactions.

The most important industrial ketone is *acetone*, $(CH_3)_2CO$. It is used in the manufacture of explosives, quick-drying laquers and enamels, plastics, paint removers, and drugs. Most fingernail polish removers contain acetone as the main solvent.

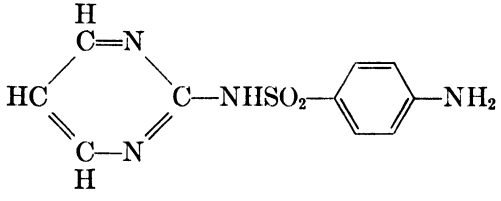
22.22 Amines. Amines contain the functional group $—NH_2$, known as the *amino* group. They have the general formula RNH_2. They may be looked upon as derivatives of ammonia in which hydrogen has been replaced by an alkyl or aryl group.

The simple aliphatic amines, methyl amine (CH_3NH_2), ethyl amine ($C_2H_5NH_2$), and propyl amine ($C_3H_7NH_2$) give the characteristic odor to fish and fish oil.

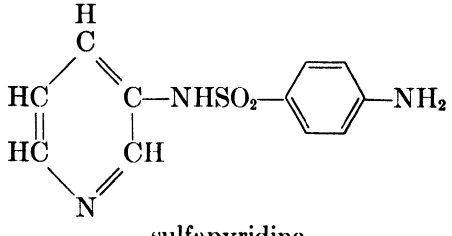
Aniline, $C_6H_5NH_2$ (phenyl amine), is the starting material in the manufacture of hundreds of *aniline dyes*. The widely used *sulfa drugs* are all complex amines.



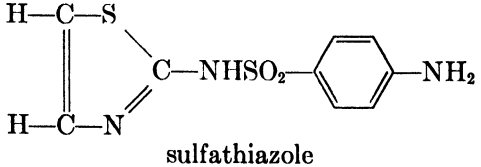
sulfanilamide



sulfadiazine

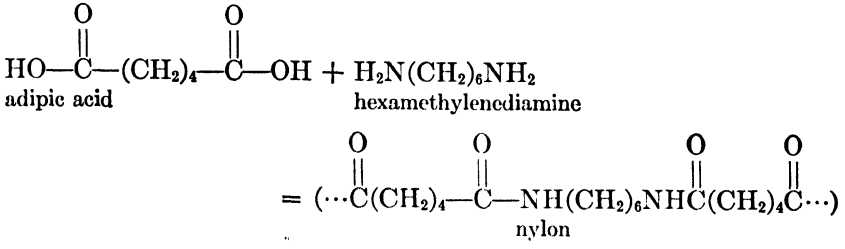


sulfapyridine



sulfathiazole

Nylon is formed by the reaction of the amine hexamethylenediamine, $NH_2(CH_2)_6NH_2$, with adipic acid. The molecules of the product of the reaction polymerize to form long chains that give nylon its characteristic properties as a plastic.



22.23 Carbohydrates. They are compounds containing carbon, hydrogen, and oxygen in which the H and O are present in the proportion in which they exist in water. All carbohydrates contain several OH groups. Some of the better known carbohydrates and carbohydrate derivatives are:

1. *Sugars:* sucrose (ordinary sugar), $C_{12}H_{22}O_{11}$; glucose or dextrose (corn syrup), $C_6H_{12}O_6$; fructose (fruit sugar), $C_6H_{12}O_6$. Sucrose is obtained from the juice of sugar cane and sugar beets. Glucose is prepared by hydrolysis (in the presence of acid) of corn starch:

$$(C_6H_{10}O_5)_x + x\,H_2O = x\,C_6H_{12}O_6.$$

2. *Starch,* $(C_6H_{10}O_5)_x$. The structures of starch and cellulose are very complex.

3. *Cellulose,* $(C_6H_{10}O_5)_x$. Cotton, linen, wood pulp, and paper are nearly pure cellulose.

Nitrocellulose (*gun cotton, smokeless powder*) is prepared by treating cellulose with a mixture of concentrated nitric and sulfuric acids under such conditions that most of the hydroxyl groups in the cellulose molecule are nitrated (converted to NO_2 groups). The less highly nitrated product is called *pyroxylin;* it was at one time used as a plastic. Because of its highly inflammable character its use as a plastic has been greatly reduced. *Collodion* is a solution of pyroxylin in ether.

Celluloid is prepared from pyroxylin. Like pyroxylin it is very inflammable.

Rayon is a type of regenerated cellulose in which wood pulp or cotton is first dissolved in sodium hydroxide and carbon disulfide to form a substance known as cellulose xanthate. When a solution of this xanthate (known as *viscose*) is extruded as a fine stream into an acid solution, fine threads of regenerated cellulose (*rayon*) are formed. If the viscose is extruded in sheets the product is known as *cellophane.*

22.24 Proteins. Proteins are very complex substances containing carbon, hydrogen, oxygen, and nitrogen, and sometimes sulfur and phosphorus. On hydrolysis they yield mixtures of *amino acids*. Amino acids are organic acids in which amino groups (—NH_2) have been substituted for one or more of the H atoms in the R group of the acid. The simplest amino acid is *glycine* (aminoacetic acid) NH_2CH_2COOH. About 25 different amino acids have been isolated from proteins. Certain of these amino acids are essential to life but cannot be synthesized in the body and must therefore be present in the diet.

Among the important proteins are globulin (in blood), hemoglobin (in blood), albumin (in egg white), gliadin and glutenin (in wheat), casein (in milk), collagen (in connective tissue and bones), keratin (in hair, wool, and horn), and certain virus proteins (influenza virus, tobacco mosaic virus).

Questions

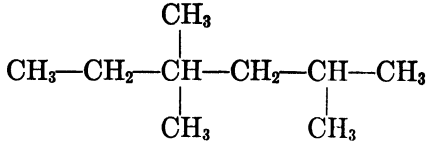
1. Distinguish between (a) saturated and unsaturated hydrocarbons; (b) alkanes, alkenes, and alkynes; (c) aliphatic and aromatic compounds; (d) alkyl and aryl groups; (e) monomer and polymer.

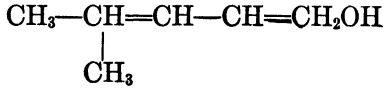
2. Define or describe and illustrate each of the following: (a) functional group; (b) hydrocarbon; (c) alkyl halide; (d) alcohol; (e) organic acid; (f) ester; (g) ether; (h) aldehyde; (i) ketone; (j) acid anhydride; (k) amine; (l) carbohydrate; (m) protein; (n) fatty acid; (o) fat; (p) soap; (q) saponification; (r) isomers; (s) fermentation; (t) amino acid.

3. For what class of compounds is each of the following the general formula?

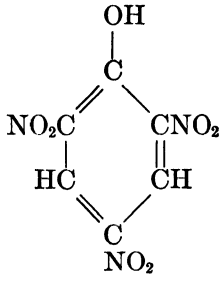
(a) R—OH; (b) R—X; (c) $R—NH_2$; (d) $R_2{=}O$; (e) R—CHO; (f) R—COOH; (g) $R_2C{=}O$; (h) RCOOR; (i) R—X; (j) $(RCO)_2O$; (k) R—H.

4. Name the following:

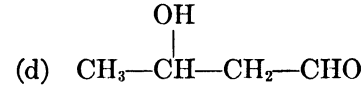
(a)


(b)


(c)



(d)



5. Give one source of each of the following: (a) methyl alcohol; (b) methane; (c) acetylene; (d) ethylene; (e) ethyl alcohol; (f) glycerine; (g) albumin; (h) soap; (i) benzene; (j) toluene; (k) sucrose; (l) glucose.

6. Write the structural formulas for each of the following:
   (a) 2,2,3,3-tetramethylhexanol.
   (b) 4-methyl-1-heptene.
   (c) 2,4,6-trinitrotoluene.
   (d) 3-methylbutanoic acid.

CHAPTER 23

Silicon

23.1 Occurrence. Silicon is the second most abundant element, and makes up about 27% of the earth's crust. Practically all the abundant components of the earth's crust except limestone and marble are silicon compounds. It occurs largely as clay [$Al_2Si_2O_5(OH)_4$], sand (SiO_2), quartz (SiO_2), feldspar ($KAlSi_3O_8$, $NaAlSi_3O_8$, $CaAl_2Si_6O_{16}$, etc.) and granite (mixture of quartz and feldspars).

23.2 Properties (see Table 21.1). Silicon is similar to carbon in its physical and chemical properties (see 21.1). It is relatively inactive at low temperatures, but at high temperatures it reacts as a typical nonmetal, combining with oxygen, the halogens, carbon, and active metals to form binary compounds. It has the unique property of reacting with strong alkalies to liberate hydrogen.

$$4\,Na^+ + 4\,OH^- + Si = 2\,H_2 + 4\,Na^+ + SiO_4^{----}\ \text{(orthosilicate ion)}$$

It does not combine directly with hydrogen, but a long series of hydrogen compounds (silanes) can be prepared by indirect methods. The silanes are analogous to the hydrocarbons and illustrate the ability of silicon atoms to combine with each other by a covalent linkage to form long-chain compounds.

Its principal oxidation states are -4 (in SiH_4 and the metal silicides) and $+4$ (in SiO_2 and the silicates). SiO exists; like CO, it is a strong reducing agent.

23.3 Commercial preparation. Silicon is prepared by reduction of SiO_2 with carbon (coke) in the electric furnace at a temperature of about 2200°C (see Figure 23.1).

$$SiO_2 + 2\,C = Si + 2\,CO$$

23.4 Commercial uses. It is used primarily for the manufacture of alloys of iron, aluminum, copper, and manganese (see 25.13), and as a deoxidizer in the refining of metals (see 25.11). The presence of silicon in alloys increases their resistance to corrosion. It increases the hard-

ness of aluminum and copper alloys and makes them easier to work in lathes and milling machines. In metal refining it reduces any metal oxide to metal, being itself converted to the oxide, which is removed as *slag*.

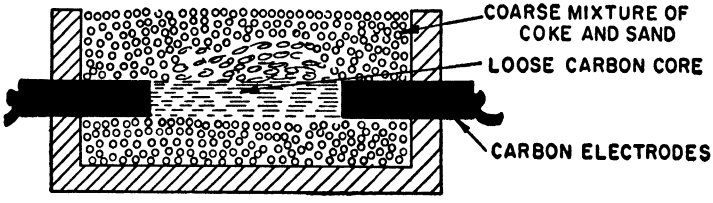


Figure 23.1. Resistance-type electric furnace used for the manufacture of silicon and silicon carbide. Because of the high electrical resistance of the loose carbon core its temperature rises to 1500–2000°C when high-voltage current is passed through it.

23.5 Some important silicon compounds and their uses

1. *Silicon dioxide*, SiO_2. It occurs in nature in the form of sand, quartz, flint, agate, opal, amethyst, and onyx. It is used for the manufacture of silicon, fused quartz glass, pyrex glass, window glass, carborundum (SiC), sodium silicate, silica gel, and abrasives. The extreme hardness of flint was the basis for its early use in flintlock rifles, and with steel, for starting fires. The tiny bits of iron that are removed by contact with the hard flint are raised to their ignition temperature by the heat of friction. A shower of sparks of burning iron is thus produced.

2. *Silicon carbide*, SiC (carborundum). It is prepared by reduction of SiO_2 with coke in the electric furnace. The method is the same as that used for preparation of silicon (23.3) except that an excess of coke is used.

$$SiO_2 + 3\,C = SiC + 2\,CO$$

It is used almost exclusively as an abrasive in the form of carborundum grinding wheels, grinding dust, whetstones, and carborundum paper. Its use as an abrasive depends upon its extreme hardness. About 65,000 tons are produced annually in the United States.

3. *Sodium silicate*, Na_2SiO_3 (water glass). It is prepared by fusion of SiO_2 with Na_2CO_3 or NaOH.

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2$$
$$SiO_2 + 2\,NaOH = Na_2SiO_3 + H_2O$$

It is used chiefly for the manufacture of soap and silica gel, as an adhesive in the manufacture of paper boxes and cartons, and as a protective coating for wood, plaster, and cement.

Its presence in soap aids in stabilizing the foam that is produced when sudsing occurs.

Silica gel is prepared by treating a solution of Na_2SiO_3 with a strong acid. A *gel* of silicic acid is formed as a result of the reaction

$$SiO_3^{--} + 2\,H^+ + H_2O = H_4SiO_4 \text{ (orthosilicic acid)}$$
$$SiO_3^{--} + 2\,H^+ = H_2SiO_3 \text{ (metasilicic acid)}$$

When this gel is dehydrated (dried out) by heating there is formed an extremely porous product called *silica gel*, consisting largely of SiO_2.

$$H_2SiO_3 \text{ (heated)} = SiO_2 + H_2O$$

Because of its great porosity and consequent large amount of surface per unit mass, silica gel has very high capacity for adsorbing moisture and other vapors. It finds extensive use as a drying agent. Great quantities are used in the petroleum industry for adsorbing vapors from natural gas; these vapors can be driven off and recovered by heating the spent gel, and the gel can then be used over again.

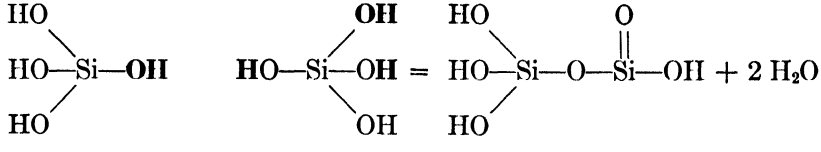
4. *Silicon tetrachloride.* It is prepared by direct combination of silicon and chlorine at high temperatures.

$$Si + 2\,Cl_2 \text{ (heated)} = SiCl_4$$

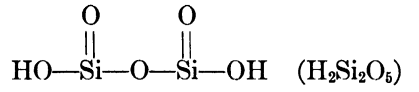
It is used by the armed forces for production of smoke screens. When mixed with water vapor and ammonia it hydrolyzes strongly and yields a smoke consisting of NH_4Cl and H_4SiO_4.

$$SiCl_4 + 4\,H_2O = \mathbf{H_4SiO_4} + 4\,HCl$$
$$NH_3 + HCl = \mathbf{NH_4Cl}$$

23.6 The condensed silicic acids. Among the silicate minerals are substances with compositions represented by such formulas as $KAlSi_3O_8$ (feldspar), $KAlSi_2O_6$ (leucite), $Be_3Al_2Si_6O_{18}$ (beryl), and $CaMg_3Si_4O_{12}$ (tremolite). These compounds may be considered to be salts of *condensed silicic acids.* Condensed acids are formed by the loss of water from 2 or more molecules of the *ortho* (H_4SiO_4) or *meta* (H_2SiO_3) acid. Thus 2 molecules of H_4SiO_4 will lose 2 molecules of H_2O and yield a disilicic acid, $H_4Si_2O_6$. In the process two atoms of Si are linked together by an atom of oxygen.

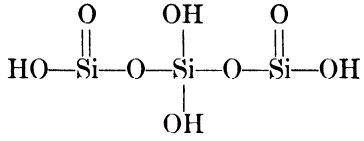


The loss of an additional molecule of H_2O will yield



$(H_2Si_2O_5)$

Similarly, 3 molecules of H_4SiO_4 can lose 4 molecules of water to give the trisilicic acid $H_4Si_3O_8$.

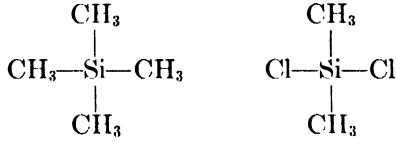


Successive steps in the dehydration process can be represented by the equation

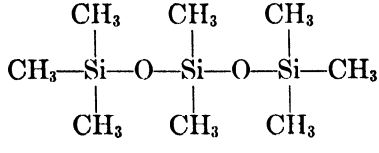
$$3\ H_4SiO_4 \xrightarrow{-2\ H_2O} H_8Si_3O_{10} \xrightarrow{-H_2O} H_6Si_3O_9 \xrightarrow{-H_2O}$$
$$H_4Si_3O_8 \xrightarrow{-H_2O} H_2Si_3O_7 \xrightarrow{-H_2O} 3\ SiO_2$$

Higher condensed acids may be formed in an analogous manner from 4 or more molecules of H_4SiO_4. Thus $KAlSi_3O_8$ is a salt of $H_4Si_3O_8$, $KAlSi_2O_6$ is a salt of $H_4Si_2O_6$, $Be_3Al_2Si_6O_{18}$ is a salt of $H_{12}Si_6O_{18}$, and $CaMg_3Si_4O_{12}$ is a salt of $H_8Si_4O_{12}$. It should be noted that pure condensed silicic acids have never been isolated; only the salts are known.

23.7 The silicones. Since silicon and carbon are so similar to each other, it is not surprising to find that an atom of one will join to an atom of the other in the same way that atoms of each separate element will link together. This gives rise to compounds such as $Si(CH_3)_4$ and $SiCl_2(CH_3)_2$ whose structural formulas are



When this ability of Si to link to C, and the capacity of an oxygen atom to link together 2 atoms of Si, noted in 23.6, are both employed in the same compound, substances of the type represented by the following formula are obtained.



These substances are called *silicones*. The particular silicone represented above is a *methyl silicone*. Higher hydrocarbon radicals such as *ethyl* (C_2H_5—), *propyl* (C_3H_7—) etc. may be substituted for CH_3, and the length of the chain may be increased.

The physical properties of the silicones vary with the length of the chain and the composition of the hydrocarbon radicals. Those of short length and lower molecular weight are oily liquids; as the chain length increases, the viscosity of the liquid increases until the long-chain compounds are solid or semisolid resinous substances.

Silicone oils have the unique property of showing very little change in viscosity with change in temperature. For that reason they are widely used where uniform viscosity over a wide range of temperatures is desirable, in hydraulic brake fluids and lubricating oils for automobiles and trucks, for example. The resinous silicones are used in making a type of synthetic rubber substitute for use in making gaskets, electrical insulation, and molded articles. These resinous materials, like the silicone oils, are stable at temperatures up to 400 and 500°C. A silicone film applied to cloth, plastics, leather, paper, wood, etc. makes them water repellant. The commercial production of silicones has shown a spectacular rise since their relatively recent discovery.

23.8 Some important products prepared from silica and silicates

1. *Window glass* is prepared by fusing together a mixture of sand (SiO_2), limestone ($CaCO_3$), and soda ash (Na_2CO_3). The fused product is a complex mixture of SiO_2, $CaSiO_3$, and Na_2SiO_3, containing about 72% SiO_2, 14% Na_2O, 13% CaO, and 1% Al_2O_3 and Fe_2O_3. Its outstanding physical property is the fact that on cooling it does not crystallize at a definite temperature. Instead, its viscosity gradually increases until finally it becomes a rigid mass. On being heated it gradually softens and finally becomes fluid. Since it does not have a definite melting point or crystal structure it is not a true solid; it is a supercooled liquid and is called a *glass* (see Figure 23.2).

Glass of different composition for different uses is made by varying the per cent of SiO_2 and adding other acidic oxides such as B_2O_3 and As_2O_3, and basic oxides such as K_2O, PbO, and Al_2O_3. *Pyrex* glassware consists of about 80% SiO_2, 13% B_2O_3, 4% Na_2O, 0.4% K_2O, and 2.2% Al_2O_3. *Colored glass* is prepared by adding the oxides of specific metals; CoO yields blue glass, FeO green, Fe_2O_3 yellow or brown, elemental selenium red, and SnO_2 milky white. *Shatterproof glass* for use in automobiles is made by sealing two sheets of ordinary glass together with a

sheet of transparent plastic. A total of 5,150,000 tons of sand was consumed in the manufacture of glass in the United States in 1950.

2. *Quartz glass* is pure fused SiO_2. It has the following distinctive properties: (a) very hard; (b) low coefficient of expansion, as a result of which it does not crack when subjected to sudden changes of temperature; (c) high refractive index; (d) very insoluble in water and other liquids; (e) high conductivity for ultraviolet light (ordinary window glass is a poor transmitter of ultraviolet light).

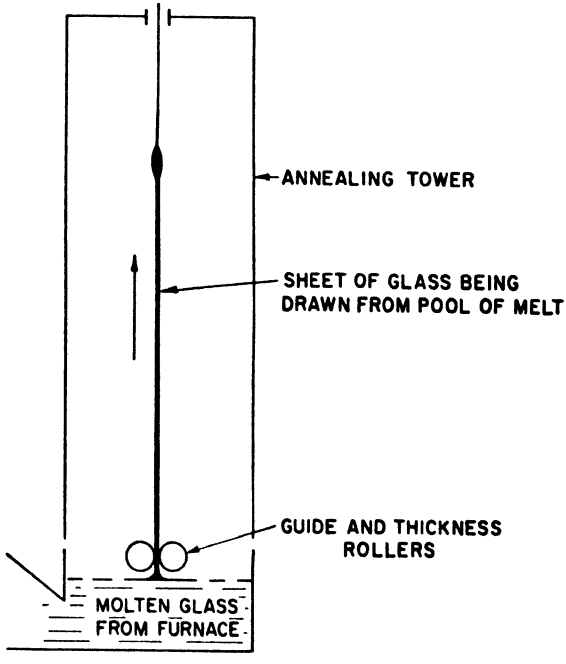


Figure 23.2. Drawing a sheet of window glass.

3. *Portland cement* is prepared by fusing together clay and limestone (see Figure 23.3). The fused product is a complex mixture of calcium silicates, calcium aluminates, aluminum silicates, and silica. Its unique property is its ability to set to a hard rocklike mass when treated with water; the reactions involved are complex. This property is the basis for its extensive use in the making of concrete and concrete products. The annual production in the United States of about 45,000,000 tons of Portland cement identifies it as one of our most important manufactured products.

4. *Brick, tile, pottery, and porcelain.* These materials are all made

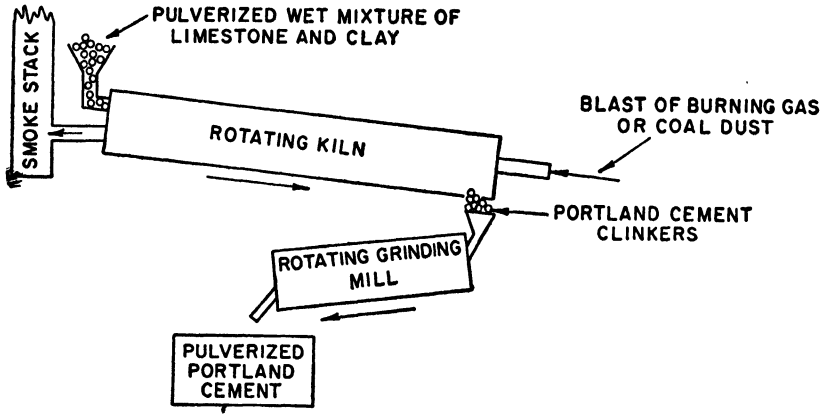


Figure 23.3. Diagram of process for the manufacture of portland cement from limestone and clay.

from clay, by mixing it with enough water to form a doughlike mass, molding into the desired shape, and baking in a furnace until the desired hardness and amount of surface sintering (melting) is attained. Brick and tile are made from relatively impure clay, and owe their characteristic red color to the presence of Fe_2O_3; other metallic compounds give other colors.

White pottery and *porcelain* are made from the best grade of pure clay, called *kaolin*. Inclusion of varying amounts of pulverized quartz, ground feldspar, and bone ash yields products of different texture and color. The product is *glazed* with a white or transparent fusible glass and is decorated with colored glazes.

Questions

1. Enumerate the evidence showing the similarity between silicon and carbon.

2. List experimental facts that show that silicon is a nonmetal.

3. Give evidence to show that silicon is less electronegative than sulfur.

4. Show, by balanced equations, how the following can be prepared starting with SiO_2: (a) Si; (b) Na_2SiO_3; (c) SiC; (d) silicic acid; (e) silica gel; (f) $SiCl_4$; (g) SiF_4

5. List the raw materials required for the preparation of each of the following and outline briefly what takes place in the course of the preparation: (a) Portland cement; (b) window glass; (c) quartz glass; (d) red brick.

6. What are silicones and for what are they used?

7. Give the structural formulas for two condensed silicic acids and show how they are derived from the *ortho* acid.

8. Account for the strongly alkaline reaction of an aqueous solution of Na_2SiO_3.

CHAPTER 24

Colloids

24.1 The nature of a colloidal suspension. When a solution of $AgNO_3$ is mixed with a solution of NaCl, a precipitate of AgCl usually forms in accordance with the reaction

$$Ag^+ + Cl^- = AgCl$$

Under certain conditions, however, AgCl does not precipitate out when Ag^+ and Cl^- ions are brought together, even though the concentrations of Ag^+ and Cl^- are sufficiently high. Instead an opaque white *suspension* is formed. Even on long standing the system remains opaque and no precipitate settles out. Filtration does not remove any AgCl; the entire opaque system runs right through the filter paper. The opaque liquid is a *colloidal suspension* of silver chloride. It is made up of particles of silver chloride *suspended* in water; each particle is made up of a great many Ag^+, Cl^- ion pairs. The particles are not in solution and they are not precipitates; they are intermediate between the two.

Similar suspensions of small particles of practically every *insoluble* substance that will be encountered in the laboratory can be formed. The suspended particles may be solid, liquid, or gas; the suspending medium (water in the illustration above) may be solid, liquid, or gas. About the only qualification is that the suspended particles must be insoluble in the medium in which they are suspended (that means that a colloidal suspension of one gas in another can not exist, because all gases are mutually soluble in each other); the system is heterogeneous, not homogeneous.

It is obvious that a colloidal suspension of the type represented by silver chloride in water is just one of a great many types. The term *colloid* has come to refer to almost any type of *heterogeneous system* in which the *size* of the particles or the condition of the *surface* of the material influences its behavior. Thus it embraces such things as soaps, emulsions, biological fluids, plasticized materials, proteins, high polymers, adsorbed gases and liquids, gelatinous or slimy precipitates, foams, and smoke. Fog, smog, clouds, sponge rubber, plastics, milk, bread, ice cream, rose petals, and blood are all colloidal systems. Fascinating volumes have been written about colloidal systems, and year-long college

courses are devoted exclusively to their study. About all that we will do in this chapter is say a little about that type of colloidal system which is frequently encountered in the laboratory, namely, *suspensions of solids in liquids.*

24.2 Classification of solid-in-liquid colloidal systems. We have noted, in Section 23.5, that a jelly-like suspension of silicic acid is formed when an acid is added to a solution of sodium silicate. This jelly is generally so rigid that it can be cut into pieces; *because it is a rigid, or semirigid, colloidal system it is referred to as a gel.* By contrast, *a fluid colloidal suspension such as* AgCl *in water or* $Fe(OH)_3$ *in water, is called a sol.*

Silicic acid forms a gel because there is strong affinity between silicic acid molecules and water molecules; the acid is highly hydrated or *solvated.* A colloidal system in which there is strong attraction between the suspended particles and the liquid suspending medium is said to be a *lyophilic* (solvent-loving) system; one in which there is little attraction, such as a suspension of gold in water, is *lyophobic* (solvent hating).

24.3 Preparation of colloids. Since the suspended colloidal particles are intermediate in size between molecules or ions in true solution and precipitates, colloidal suspensions can be prepared by:

1. *Condensation;* starting with ions or molecules in solution and allowing them to "grow" to colloidal size.

2. *Dispersion;* starting with a large mass of the material to be suspended and breaking it down to colloidal size.

The formation of colloidal AgCl and $Si(OH)_4$ in the examples given earlier illustrates condensation. Condensation occurs whenever colloids are formed by a chemical reaction in solution.

The preparation of paint, by grinding the solid pigment in linseed oil, illustrates dispersion. Likewise, formation of muddy water by stirring a mixture of dirt and water, and of colloidal CuS by adding a solution of $(NH_4)_2S$ to solid CuS illustrates dispersion. When dispersion of a solid takes place as the result of adding a solution of an electrolyte, as when $(NH_4)_2S$ solution is added to solid CuS, and clay is dispersed in water, the process is referred to as *peptization.*

24.4 Properties of solid-in-liquid sols

1. The system is heterogeneous. It is not a true solution. The individual particles are commonly referred to as *micelles.*

2. The particles are small. Molecules generally are less than 1 millimicron in diameter; particles of diameter greater than 100 millimicrons

generally settle out as a precipitate. Therefore colloidal particles are between 1 and 100 millimicrons in diameter. (One millimicron is one one-millionth of a millimeter.)

3. The particles pass through the relatively large pores of ordinary filter paper; membranes can, however, be selected whose pores are too small to allow passage of colloidal particles but large enough to allow passage of ions and molecules in true solution. By the use of such a membrane a colloid may be separated from a true solution. This separa-

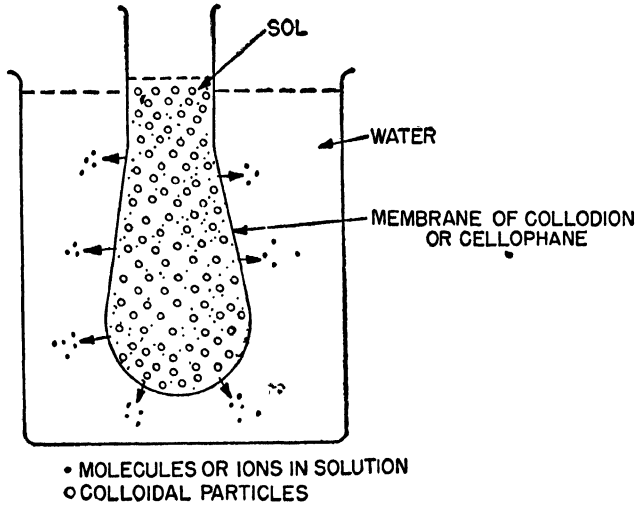


Figure 24.1. Separation of a true solution from a colloid by dialysis. The molecules or ions in solution will pass through the pores of the membrane, the colloidal particles will not. If the water in the beaker is continually renewed a sol containing a relatively small amount of dissolved substance will be formed.

tion process is called *dialysis* (see Figure 24.1). Membranes made from collodion, cellophane, parchment, and animal intestines may be used in dialysis. Dialysis is an important process in the assimilation of foods as they pass through the intestinal tract.

4. The particles show the path of a beam of light. Although the particles are too small to be visible under the microscope, they are large enough to reflect light (see Figure 24.2). Therefore, when a beam of light is passed through a colloidal suspension its path is traced by the light which is reflected (see Figure 24.3). This, incidentally, is exactly what happens when a strong beam of sunlight shines into a dust-filled room or a strong searchlight is directed into a foggy atmosphere. The

ability of colloidal particles to show the path of a beam of light is known as the *Tyndall effect.* True solutions do not show the Tyndall effect because their molecules and ions are too small.

5. The color of a colloidal suspension varies with the size of the particles and the nature of their surface. Red colloidal gold particles are smaller than those in the blue colloid.

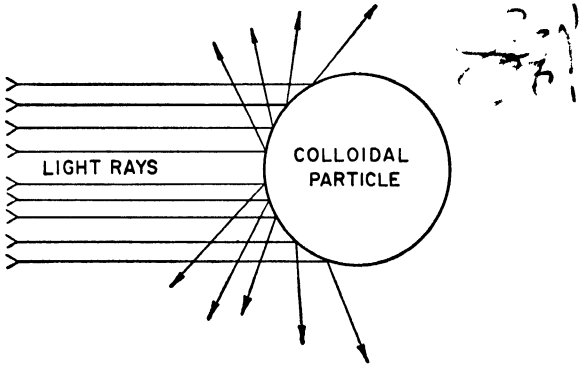


Figure 24.2. Reflection of light from the surface of a spherical colloidal particle.

6. The colloidal particles are generally visible under the ultramicroscope; this scope is a device in which the individual light points which are the cause of the Tyndall effect are magnified by observation with a

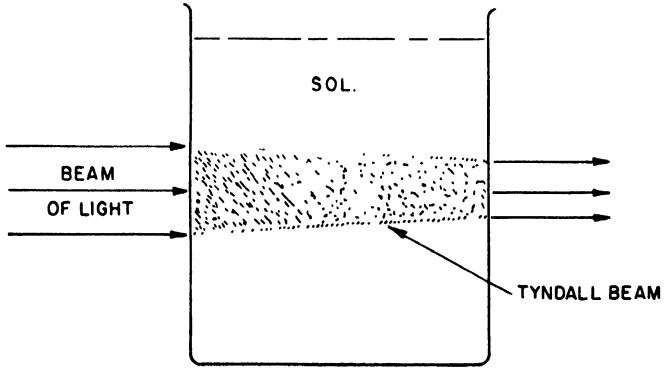


Figure 24.3. A Tyndall beam. The colloidal particles reflect light. As a result, when a beam of light is passed through a sol its path is traced by the light which is reflected. The resulting illuminated area is called a Tyndall beam.

standard microscope (see Figure 24.4). Just as you see the light reflected from a planet, not the planet itself, so under the ultramicroscope you see the light that is reflected by a particle, not the particle itself.

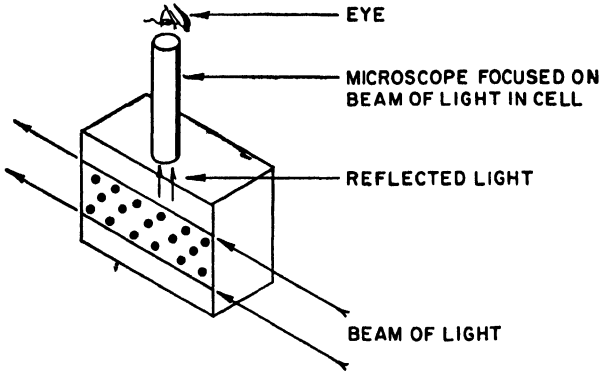


Figure 24.4. Observation of colloidal particles with the aid of a microscope. The scope magnifies each light point that results when light is reflected by the particle.

7. The particles in a sol are continually moving about as a result of their bombardment by solvent molecules. This is known as *Brownian movement.*

8. The surfaces of all particles in a given sol carry like electric charges. These charges are due to adsorption of ions on the surface of the particle (see Figure 24.5). It is this like charge on each particle that causes them to repel each other and keeps them from becoming large enough to form precipitates.

The following experimental facts, in addition to the observation that the particles repel each other, show that the particles carry like charges.

(a) The particles in a given sol will migrate to one pole when a current is passed through it. This mass migration of colloidal particles is called *electrophoresis* or *cataphoresis* (see Figure 24.6). Colloidal $Fe(OH)_3$ migrates to the negative pole; the particles are therefore positively charged (due to adsorption of Fe^{+++} ions). Colloidal As_2S_3 moves to the positive pole; the particles must be negatively charged (due to adsorption of S^{--} ions).

(b) The particles in a negative sol and those in a positive sol will mutually *coagulate* (precipitate) each other. Thus when $Fe(OH)_3$ and As_2S_3 sols are mixed, a precipitate is formed; this precipitate can be shown to be a mixture of As_2S_3 and $Fe(OH)_3$. When the two sols are brought together, the oppositely charged ions on the two sets of particles neutralize each other, and the entire system is precipitated out.

(c) Sols can be coagulated by electrolytes. When Na_2SO_4 solution is added to a suspension of $Fe(OH)_3$, coagulation takes place and a precipitate of $Fe(OH)_3$ is formed. The negative SO_4^{--} ions neutralize the positive charges on the particles. As a result they are able to unite to form a precipitate.

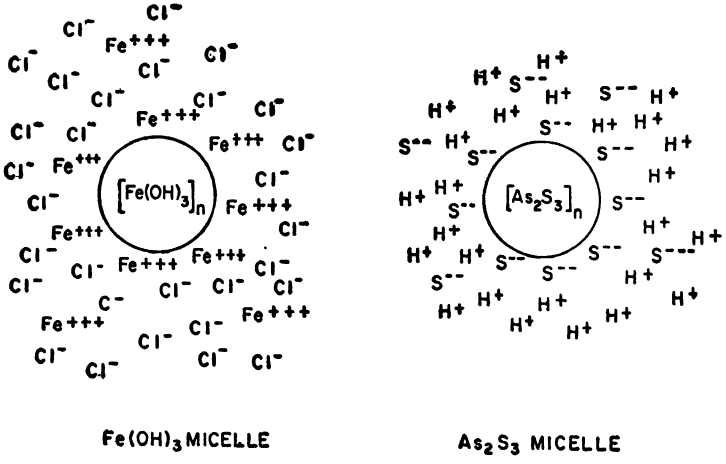


Figure 24.5. Adsorption of ions by colloidal particles. Each micelle in a $Fe(OH)_3$ sol carries a positive charge due to adsorbed Fe^{+++} ions. Each micelle in an As_2S_3 sol carries a negative charge due to adsorbed S^{--} ions. Since each sol is neutral, for every ion adsorbed on the particles an equivalent number of ions of opposite charge is present in the solution.

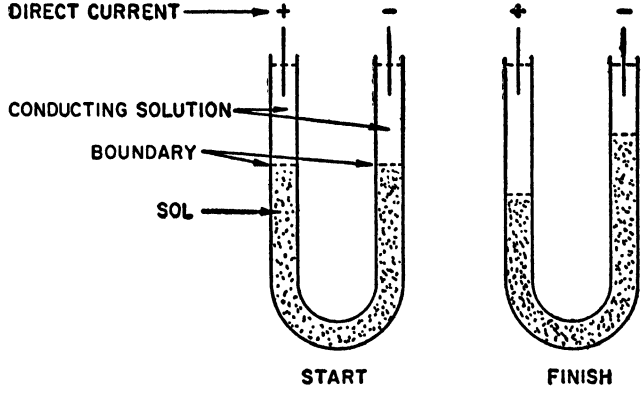


Figure 24.6. Cataphoresis of a ferric hydroxide sol. The mass migration of the micelles away from the positive electrode and toward the negative electrode, as evidenced by the movement of the boundary between the conducting solution and the sol, shows that the particles are positively charged.

The choice of the ion that is adsorbed by a specific micelle when the colloid is formed appears to be determined by the following rules.

(a) It will preferentially adsorb the ion of the same species of element as is contained in the particle. Thus $Fe(OH)_3$ particles will preferentially adsorb Fe^{+++} and OH^- ions.

(b) It will preferentially adsorb from among ions of the correct species the one with the greatest charge. Thus $Fe(OH)_3$ will adsorb Fe^{+++} rather than OH^-, and $Fe(CN)_6^{----}$ rather than Fe^{+++}.

(c) From among ions with the same number of charges and of the correct species, it will adsorb the one whose concentration is highest. Thus AgCl will adsorb either Ag^+ or Cl^-, whichever is present in the higher concentration.

The sign of the charge on the particles in the sol can be determined by:

(a) Electrophoresis. This is generally carried out in a U-shaped tube, using platinum electrodes.

(b) Testing the sol with another sol of known charge to see whether or not mutual coagulation will occur. A negative sol will coagulate a positive sol but will not normally coagulate another negative sol.

(c) Adding a series of electrolytes containing different positive and negative ions. The greater the charge on an ion, the greater the coagulating power toward a sol of opposite charge. Suppose exactly equal amounts of 0.1 *N* KCl, 0.1 *N* K_2SO_4, and 0.1 *N* K_3PO_4 were required to coagulate 10 ml portions of a given sol. That means that the same ion must have done the coagulating in each instance. The common ion in each of the three electrolytes is the K^+ ion. Therefore the sol must have been negative. If, in another case, the coagulation of 10 ml portions of a sol required, respectively, 2 drops of 0.1 *N* K_3PO_4, 20 drops of 0.1 *N* K_2SO_4, and 4 ml of 0.1 *N* KCl, one would conclude that different ions were responsible for the coagulation. The different ions are PO_4^{---}, SO_4^{--}, and Cl^-. Therefore the sol must have been positive.

Coagulation of colloids by addition of specific electrolytes is of great practical importance in many laboratory operations involving precipitation.

9. The micelles have high particle weights. They are in a sense giant molecules. Because of their high particle weights and the fact that they are in reality not in solution, they have only negligible effects on the boiling point and freezing point of the solvent. Likewise, being giant molecules, the micelles diffuse very slowly.

10. The particles have great adsorbing power toward ions and other solutes. This is because they are small and have therefore a high ratio of surface to mass. It is this great adsorbing power that is responsible

for the initial adsorption of ions and the consequent formation of a colloidal system.

24.5 Protective colloids. If a suspension of a lyophilic colloid such as gelatin or agar is added to a sol such as ferric hydroxide in water, the latter will not be coagulated by an amount of K_2SO_4 that will normally cause coagulation. The gelatin acts as a *protective colloid.* It stabilizes the sol, probably by adsorbing $Fe(OH)_3$ micelles or being adsorbed by them. In so doing it contributes its hydrophilic character to the $Fe(OH)_3$ particle and makes it more difficult to coagulate. Stabilization of hydrophobic sols by hydrophilic micelles is of importance in the preparation of industrial and pharmaceutical suspensions.

24.6 The structure of gels. To be capable of forming a gel in water, a substance must be strongly hydrophilic. Also, its molecules must be capable of combining with each other to form a netlike structure of chains and cross links. The hydrophilic character and the tendency to interlink increase as the temperature decreases. As a result, when a fluid dispersion of such a substance in warm water is cooled, it sets to a rigid or semirigid gel. If the gel is warmed, its rigidity disappears and it becomes a sol. The structure of a gel is probably similar to what would exist if an intricate cross-linked spider web were woven in a beaker full of water or if a hair net were tucked into a small beaker of water. Gelatin desserts are typical gels.

24.7 Emulsions. The term *emulsion* is applied to any system in which one liquid is colloidally dispersed in another. An *emulsifying agent* is generally necessary to give a stable emulsion; it is in a sense a protective colloid. Thus a hydrophilic soap suspension will act as an emulsifying agent and stabilize an emulsion of oil in water.

Questions

1. Define or describe and illustrate: sol; gel; condensation; dispersion; adsorption; lyophobic; lyophilic; peptization; coagulation; cataphoresis; dialysis; electrophoresis; Tyndall effect; Brownian movement; micelle; ultramicroscope; emulsion; protective colloid; solvation; emulsifying agent.

2. Distinguish between condensation and dispersion methods for preparing colloids and give the details of preparing one colloid by each method.

3. How would you verify, by all available facts, that a yellow liquid is a colloidal suspension of As_2S_3 rather than a true solution of K_2CrO_4?

4. How would you determine, by all available methods, the sign of the charge on the particles of a sol?

5. Enumerate the evidence which leads to the conclusion that particles in a sol carry like electric charges.

6. Give all the reasons why the particles in a sol will not settle out.

7. Enumerate the general rules which determine what ion will be adsorbed by the particles of a sol.

8. Which of the following 0.1 *N* solutions would be the most effective in coagulating negative colloidal As_2S_3? Which the least effective? NaCl; $BaCl_2$; $AlCl_3$.

9. Ten ml of 0.2 *M* $AgNO_3$ and 25 ml of 0.01 *N* NaCl were brought together in 2 liters of water under such conditions that colloidal AgCl formed. What was the sign of the charge on the AgCl?

10. Which of the ions listed, when present in equivalent concentrations, would be preferentially adsorbed by the colloid listed?

(a) $Fe(OH)_3$; OH^-, Cl^-, Fe^{+++}, SO_4^{--}, $FeCl^{++}$, H^+.

(b) As_2S_3; $H_2AsO_3^-$, S^{--}, H^+, OH^-.

(c) $Fe(OH)_3$; Fe^{+++}, $Fe(CN)_6^{----}$, Fe^{++}, OH^-.

11. To coagulate 10 ml samples of a certain lyophobic sol required, respectively, 4 ml of 0.1 *N* $BaCl_2$, 10 ml of 0.04 *N* NaCl, 2 ml of 0.2 *N* $AlCl_3$, 1 ml of 0.01 *N* Na_2SO_4, and 2 drops of 0.002 *N* Na_3PO_4. What was the sign of the charge on the particles of the sol?

CHAPTER 25

The Metals

The metals have been referred to repeatedly in the preceding chapters, but in every instance they have served as accessories in the presentation of some concept, as in the discussion of the periodic table, the structure of the atom, and acids, bases, and salts, or in the detailed elaboration of the properties of certain nonmetals. The remaining chapters will be devoted specifically to a discussion of the important features of the chemistry of the common metals. The general properties of all metals will be discussed in this chapter; specific metals will be taken up in the chapters that follow. Although much of the material presented in this chapter will have been mentioned before, it is summarized here so as to give a complete picture.

Inasmuch as the principles underlying the chemistry of the metals have already been presented in earlier chapters, most of the material that follows will be essentially descriptive. For that reason it can be presented largely in semioutline form.

Only the more common metals will be considered in this book. They will be taken up in the order in which they are encountered in most of the procedures used for analysis of the cations. Within this order, however, they will be considered in groups as they appear in the periodic table.

25.1 Importance of the metals. Seventy-eight of the 100 elements are classed as metals. They fall to the left and below the zigzag line that is drawn below elements H, B, Si, As, Te, and A in the periodic table.

Metals and their alloys are the major structural materials used in building the machinery and equipment for our modern civilization. The quantity of iron and steel that is being produced is one of the best indexes to our national prosperity.

25.2 Electronic configuration of the atoms of the metals

Most metals have 1, 2, or 3 electrons in their valence shell; some have 4 or more (see Figure 7.6, page 144). These electrons are relatively loosely attached and have a high degree of freedom and mobility. Be-

cause these electrons are loosely attached they tend, as a general rule, to be given off (transferred) when the metal reacts, thereby forming positive ions (cations). Most of the characteristic physical and chemical properties of a metal and the variations in these properties with atomic number and position in the periodic table can, we shall find, be interpreted in terms of the electronic configuration of the atom.

25.3 Categories in which specific metals are placed

Light metals are the metals whose densities are less than about 4; included are aluminum and the metals of groups IA and IIA. They have relatively large atomic diameters.

Heavy metals are the metals whose densities are greater than 4. This category includes all metals except the light ones. They have relatively small atomic diameters and high atomic weights. As a rule they are relatively hard.

Noble metals include the familiar metals mercury, silver, gold, and platinum, and the less familiar ruthenium, rhodium, palladium, osmium, and iridium. They have low oxidation potentials and low reactivity. The name of the category is emblematic of the fact that, because of their inactivity, they are not easily tarnished.

Base metals include all metals except the noble ones.

Alkali metals are the metals of group IA. Their hydroxides are strong bases.

Alkaline earth metals are the metals of group IIA. Their hydroxides are moderately strong bases.

Transition metals are the metals in groups IIIB, IVB, VB, VIB, VIIB, and VIIIB; their atoms have unfilled inner subshells. (Some chemists include the IB elements in the transition series, some include the IB and IIB elements. What is included depends on how the term *transition metal* is defined.)

The metalloids. This category includes aluminum, antimony, chromium, gallium, germanium, lead, tin, and zinc. Their hydroxides are amphoteric in character. They fall along the zigzag diagonal borderline between the nonmetals in the upper right-hand corner of the table and the metals in the rest of the table.

25.4 Physical properties of the metals. As a general rule:

1. They have a characteristic bright "metallic" luster when polished. This luster is believed to result from the fact that the electrons, being loosely bound and mobile, readily absorb light and re-emit it rather than transmitting it to adjacent atoms.

2. They are ductile and malleable. Ductility is the capacity for being drawn out into a relatively fine wire. Malleability is the capacity for being pounded into a thin sheet. Possession of these two properties means that metals are capable of undergoing *plastic flow*. A metal can undergo plastic flow because the loosely bound electrons are free to move from one atom to another. As a result, the metal can be distorted without loss of rigid structure. The strong but flexible and adjustable force that holds the metal atoms together is referred to as *metal bonding*. By contrast, nonmetals have nonelastic, nonadjustable covalent bonding, and are accordingly brittle, nonmalleable, and nonductile and do not undergo plastic flow.

3. They have high tensile strength. Because of the strong metal bonding and the mobility of the electrons, metals have high resistance to fracture.

4. They are excellent conductors of electricity and heat. This is accounted for by the fact that the electrons, being relatively loosely bound and not necessarily attached to a specific atom, are free to move easily from one atom to another. These moving electrons conduct the heat and electricity.

25.5 Chemical properties of metals

1. Their atoms tend, as a rule, to lose electrons to form positive ions (cations). Hence they are said to be *electropositive*. The oxidation potential ($E°$) of the reaction, metal = cation + electron, is a measure of the ease with which the metal loses its electrons; it is a measure of its electropositivity. An element which is strongly electropositive has a high oxidation potential; that means that it readily loses electrons to form a positive ion.

$$\mathrm{K} = \mathrm{K^+} + e \qquad E° = 2.925 \text{ volts}$$
$$\mathrm{Zn} = \mathrm{Zn^{++}} + 2e \qquad E° = 0.763 \text{ volt}$$
$$\mathrm{Cu} = \mathrm{Cu^{++}} + 2e \qquad E° = -0.337 \text{ volt}$$

2. They are base-forming elements. Their oxides and hydroxides are basic in character. The hydroxides of the group IA and IIA metals are the strongest bases. These metals are also the most strongly electropositive.

3. They are reducing agents. The reaction, metal = cation + electron, is an oxidation-reduction reaction in which the metal functions as a reducing agent. The reducing strength of a metal is indicated by its position in the table of oxidation potentials (see Table 20.1). The higher the potential, the greater the reducing power.

4. They combine with the electronegative nonmetals by transfer of electrons to form electrovalent salts. This is a method for preparing a salt.

$$Mg + Cl_2 = MgCl_2$$
$$Fe + S = FeS$$

5. The metals with positive oxidation potentials, indicating that they are more electropositive than hydrogen, will react with dilute acids to liberate hydrogen and form salts (solutions containing the cations of the metal). The higher the potential of the metal the more rapidly the hydrogen will be liberated.

$$Mg + 2\,H^+ = Mg^{++} + H_2$$

6. All metals dissolve in aqua regia to form a solution of the simple cation or complex chloro ion. The metals of groups IA and IIA form simple cations; these metals show very little tendency to form complex ions. All other metals form complex chloro ions.

$$3\,Ca + 8\,H^+ + 2\,NO_3^- = 3\,Ca^{++} + 2\,NO + 4\,H_2O$$
$$3\,Zn + 2\,NO_3^- + 12\,Cl^- + 8\,H^+ = 3\,ZnCl_4^{--} + 2\,NO + 4\,H_2O$$

7. The base metals (those more electropositive than mercury) react with heated oxygen or air to form the oxides of the metals. ($2\,Cu + O_2 = 2\,CuO$). The noble metals do not combine with oxygen when heated to a high temperature.

8. A metal will replace (reduce) from solution a metal of lower oxidation potential (see Table 20.1).

$$Zn + Cu^{++} = Zn^{++} + Cu$$

9. The metals of groups IA and IIA form compounds in which they exhibit only one state of oxidation; with a few exceptions, the metals in all other groups exhibit, in their compounds, more than one oxidation state. As the oxidation number of such an element increases, its oxide becomes less basic and more acidic in character. The high oxidation state compounds or ions generally can function as oxidizing agents.

$$2\,MnO_4^- + 5\,Sn^{++} + 16\,H^+ = 2\,Mn^{++} + 5\,Sn^{++++} + 8\,H_2O$$

10. Metals are deposited at the negative pole (cathode) when solutions of their salts or bases are electrolyzed. Their ions are positively charged (cations).

$$Zn^{++} + 2e = Zn$$

25.6 Relation between the properties of a metal and its position in the periodic table. In general as you move to the left in the

periodic table, the oxides and hydroxides of the metals become more basic, and the oxidation potential of the reaction, metal = cation + electron, increases. The most electropositive metals fall in groups IA and IIA.

In groups IA and IIA, as the atomic number increases, the electropositivity of the metal increases. No such orderly relationship is observed in the B groups (see 25.5–9).

25.7 Unique properties of the transition metals

1. They have incomplete subshells below the valence shell (see Table 7.3 and Figure 7.6).

2. They exist in ions and compounds in different oxidation states (see Figure 7.14). This is in sharp contrast to the group IA and IIA metals that show only one oxidation number. This tendency to exist in different oxidation states is probably related to the fact that their atoms have unfilled inner subshells.

3. They show a strong tendency to form complex ions, including hydrated (aquo) ions. Their small diameters and the incompleteness of their inner subshells are probably the important factors that cause them to form complex ions more readily than do the other metals. It should be noted, however, that the group IB and IIB metals do form many complex ions even though they are not ordinarily classed as transition metals.

4. They form colored ions, largely because of the presence of incomplete inner subshells. The ions of other metals are as a rule colorless.

5. They have small atomic diameters (see Figure 7.7).

6. They are dense and hard, with high melting points (see Figure 7.8).

25.8 Salts

1. All salts have an ionic crystal lattice. The constituents of this lattice are cations (positive metal ions) and anions (negative nonmetal or nonmetal-radical ions). The positive ion may be the cation of any metal, and the negative ion may be the anion of any nonmetal or nonmetal radical (in anions such as CrO_4^{--} and MnO_4^- the Cr and Mn are in reality acting as nonmetals). With a few exceptions any cation may form a salt with any anion. The ionic crystal lattice results from the fact that all salts are electrovalent compounds.

2. As a general rule salts are strong electrolytes; $AlCl_3$, $HgCl_2$, $CdCl_2$, and $Pb(C_2H_3O_2)_2$ are exceptions.

3. Solid salts are hard and brittle and have relatively high melting points. This results from the strong and continuous bonding that exists between the oppositely charged ionic species in the crystal lattice.

4. Being electrovalent, salts are all soluble to a greater or lesser degree in the polar solvent water. The experimentally determined rules given in Table 11.2 on page 222 cover the solubilities in water of the common salts of the common metals.

5. Salts can be prepared by the methods given in Section 13.12, page 270.

25.9 Natural occurrence of the common metals. The metals that are less reactive than calcium occur in nature largely as silicates, sulfides, carbonates, and oxides. The metals that are more reactive than magnesium never occur as oxides or sulfides; they occur as chlorides, carbonates, sulfates, and silicates. Although silicates of most metals are common they do not generally serve as a commercial source of the element (a mineral which serves as a commercial source of an element is called an *ore* of that element). The occurrence of the metals in nature can be correlated with their reactivity and oxidation potentials in the manner shown in Table 25.1. (It should be emphasized that this correlation is not exact; there are numerous exceptions.)

TABLE 25.1

REACTIVITY OF METALS

Order of reactivity as indicated by the ease of oxidation	*Form in which metals commonly occur in nature*	*Oxidation potentials* (volts)	
K	Chlorides and sulfates	$K = K^+ + e$	2.925
Na	Chlorides and sulfates	$Ba = Ba^{++} + 2e$	2.90
Ba	Chlorides and sulfates	$Ca = Ca^{++} + 2e$	2.87
Ca	Chlorides and sulfates	$Na = Na^+ + e$	2.714
Mg	Chlorides and sulfates	$Mg = Mg^{++} + 2e$	2.37
Al	Chlorides and sulfates	$Al = Al^{+++} + 3e$	1.66
Mn	Chlorides and sulfates	$Mn = Mn^{++} + 2e$	1.18
Zn	Chlorides and sulfates	$Zn = Zn^{++} + 2e$	0.763
Cr	Chlorides and sulfates	$Cr = Cr^{+++} + 3e$	0.74
Fe	Chlorides and sulfates	$Fe = Fe^{++} + 2e$	0.440
Cd	Chlorides and sulfates	$Cd = Cd^{++} + 2e$	0.403
Co	Chlorides and sulfates	$Co = Co^{++} + 2e$	0.277
Ni	Chlorides and sulfates	$Ni = Ni^{++} + 2e$	0.250
Sn	Chlorides and sulfates	$Sn = Sn^{++} + 2e$	0.136
Pb	Chlorides and sulfates	$Pb = Pb^{++} + 2e$	0.126
(H)	Chlorides and sulfates	$H = H^+ + e$	0.000
Bi	Sulfides, Carbonates, Oxides, Silicates		
Sb	Sulfides, Carbonates, Oxides, Silicates		
Cu	Sulfides, Carbonates, Oxides, Silicates	$Cu = Cu^{++} + 2e$	−0.377
Hg	Sulfides, Carbonates, Oxides, Silicates	$Ag = Ag^+ + e$	−0.799
Ag	Sulfides, Carbonates, Oxides, Silicates	$Hg = Hg^{++} + 2e$	−0.854
Au	Free element		

25.10 Metallurgy of metals (preparation of the metals from their ores). Most of the metals owe their importance to the use of the pure metal, or its alloys with other elements, in the manufacture of various structural materials. The recovery of the metal from its ores is therefore a very important industrial operation. An examination of the methods that are employed for the metallurgy of the metals shows that the choice of the method used for a particular metal is determined by the following factors:

1. The electropositivity (reactivity) of the metal.
2. The chemical composition of the ore of the metal.
3. The purity of the ore.
4. The degree of purity required in the prepared metal.
5. The presence in the ore of ores of other recoverable metals.

The manner in which each of these factors effects the choice of method can be summarized as follows:

A. *The Electropositivity (Reactivity) of the Metal*

1. The metals above manganese in reactivity (Al, Mg, Ca, Ba, Na, K) are generally prepared by electrolysis of their fused chlorides or hydroxides or, in the case of Al, by electrolysis of a solution of the oxide in a fused salt bath. Because these metals are so strongly electropositive that they react with water to liberate hydrogen and form the hydroxide of the metal, they cannot be prepared by electrolysis of aqueous solutions of their salts.

In the case of Na and K, the naturally occurring chlorides can be electrolyzed. The aluminum ore, bauxite (Al_2O_3), serves as the direct source of aluminum. The magnesium, calcium, and barium carbonates are first converted by treatment with HCl to chlorides, which are subsequently melted and electrolyzed.

2. The metals below Al in reactivity are prepared by (a) reduction of the oxide and/or (b) electrodeposition or replacement from an aqueous solution prepared by dissolving the ore in an appropriate solvent. The reduction of the oxide may be done with coke (carbon), with carbon monoxide, with aluminum, with excess sulfide ore, or just with heat.

From the standpoint of tons of metals produced, *reduction by carbon or carbon monoxide* is the most widely used metallurgical process. The important ore may be the oxide as in the case of iron (hematite, Fe_2O_3, and magnetite, Fe_3O_4), manganese (pyrolusite, MnO_2), chromium (chromite, $FeO \cdot Cr_2O_3$), and tin (cassiterite, SnO_2). In this event no roasting is necessary. If the ore is a carbonate, it is first decomposed by heating to yield the oxide, while if it is a sulfide, as is the case with a large number of metals, the ore is first roasted to give the oxide, which is then reduced with C or CO. The gaseous product of the reduction by



Figure 25.1. Metallurgical reduction plant of the Anaconda Copper Mining Company at Anaconda, Montana. This is one of the world's largest copper smelters. It also processes zinc and manganese ores and phosphate rock. (*Courtesy Anaconda Copper Mining Company*)

carbon is either CO_2 or CO. At low temperatures the gas is largely CO_2. As the reduction temperature increases, the per cent of CO increases and that of CO_2 decreases. As a general rule the greater the reactivity of the metal, the greater the stability of its oxide. The more stable the oxide, the more difficult it is to reduce it to the free metal. Therefore, as one goes up the reactivity table, the temperature required to bring about reduction increases. Above manganese the temperature required becomes so high as to make reduction by carbon or carbon monoxide impractical. For that reason the highly reactive metals are, as has already been noted, prepared by electrolysis of their fused compounds.

Some typical reactions illustrating carbon or carbon monoxide reduction are:

$$Fe_2O_3 \text{ (hematite)} + 3\,CO \text{ (heated)} = 2\,Fe + 3\,CO_2$$

$$2\,PbS \text{ (galena)} + 3\,O_2 \text{ (heated)} = 2\,PbO + 2\,SO_2$$

$$2\,PbO + C \text{ (heated)} = 2\,Pb + CO_2$$

Small amounts of Mn and Cr and a number of the less familiar metals, notably the lanthanides, are prepared by *reduction* of their oxides *with aluminum*. This method is referred to as the *Goldschmidt process*. Since aluminum is a more powerful reducing agent than any metal less electropositive than itself, it will reduce the oxides of these metals to the free metal, being itself oxidized to Al_2O_3. A typical illus-

trative reaction is

$$3\ MnO_2 \text{ (pyrolusite)} + 4\ Al \text{ (heated, to initiate reaction)} = 2\ Al_2O_3 + 3\ Mn + \text{heat}$$

Reduction with excess sulfide ore has become almost standard practice in the metallurgy of copper and lead. Using the recovery of lead from galena (PbS) as an example, a part of the sulfide is first roasted to the oxide.

$$2\ PbS + 3\ O_2 = 2\ PbO + 2\ SO_2 + \text{heat}$$

This oxide is then reduced by the excess PbS present, the reaction being largely

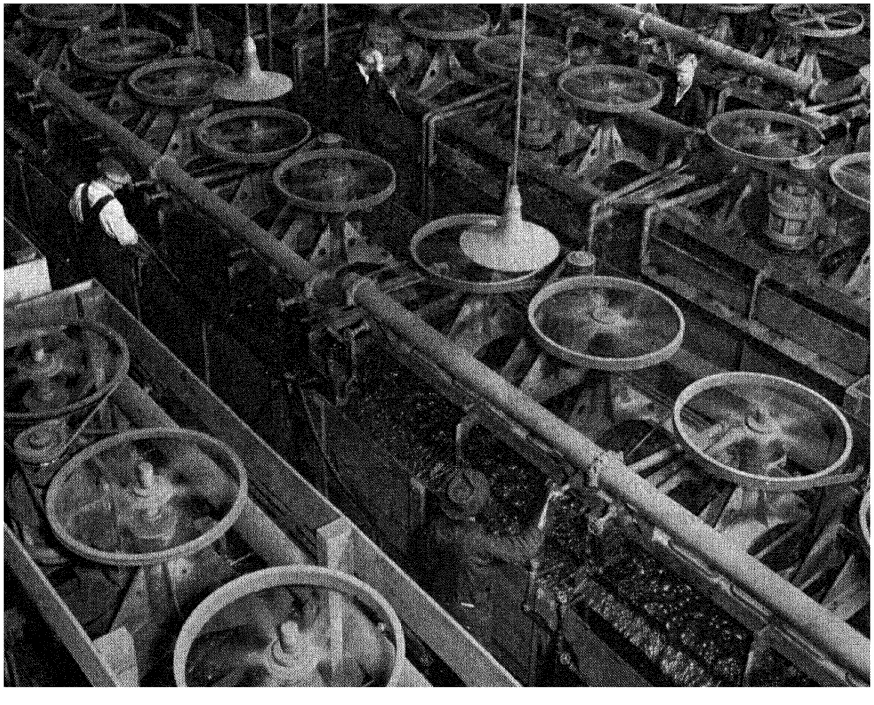
$$2\ PbO + PbS = 3\ Pb + SO_2$$

Some PbO is reduced according to the reaction

$$PbS + 4\ PbO = PbSO_4 + 4\ Pb$$

Reduction by heat (thermal decomposition of the oxide) takes place only in the case of the noble metals. Thus when mercury is prepared from the sulfide ore cinnabar (HgS), the HgO, which might presumably

Figure 25.2. Concentration of copper ore by froth flotation. Note the froth of bubbles spilling over the tops of the tanks in the foreground. This froth carries with it the copper ore; the impurities are not adsorbed by the bubbles, and hence are not carried over with the froth. (*Courtesy Anaconda Copper Mining Company*)



be formed in the roasting process according to the reaction

$$2\,HgS + 3\,O_2 = 2\,HgO + 2\,SO_2$$

is immediately reduced by heating to free Hg.

$$2\,HgO = 2\,Hg + O_2$$

The over-all reaction is represented by the equation

$$HgS + O_2\ (\text{heated}) = Hg + SO_2$$

When a metal is recovered by *electrodeposition or replacement* from aqueous solution, the ores, usually of low grade, are first leached with dilute H_2SO_4 (in the case of Zn, Cd, Cu, Mn, Cr, Co, and Ni) or a dilute solution of NaCN (in the case of Ag and Au), and the leach liquor is then electrolyzed. In the case of copper and silver, the metal may be displaced by scrap iron and zinc, respectively. Typical illustrative equations are

$$CuCO_3 + 2\,H^+ + SO_4^{--} = Cu^{++} + So_4^{--} + H_2O + CO_2$$

$$Cu^{++} + 2e\ (\text{at the negative pole of a cell}) = Cu$$

or

$$Cu^{++} + Fe = Fe^{++} + Cu$$

$$Ag_2S + 4\,Na^+ + 4\,CN^- = 2\,Ag(CN)_2^- + 4\,Na^+ + S^{--}$$

$$Zn + 2\,Ag(CN)_2^- = 2\,Ag + Zn(CN)_4^{--}$$

B. *The Chemical Composition of the Ore of the Metal.* The compound which constitutes the ore affects the metallurgical process in the following way: *Sulfide* ores must first be *roasted;* the resulting oxide is then reduced by one of the methods outlined above. *Oxide* and *carbonate* ores of metals below Al can be reduced directly with C or CO as outlined above. Ores of metals above Al are converted to fused chlorides or hydroxides and are then electrolyzed; the ore of Al is converted to a solution of purified oxide and electrolyzed.

C. *Purity of the Ore.* High-grade ores can be processed directly by an appropriate method. Low-grade ores must first be concentrated. Concentration can be accomplished by:

1. *Gravity settling* of a finely ground suspension of ore in water. The heavy ore settles to the bottom while the lighter impurities float away.

2. *Froth flotation* of a finely ground suspension of ore in water (see Figure 25.2). A stream of fine air bubbles is caused to rise through a suspension of the finely ground ore in water containing a small amount of special oils and chemicals. The particles of ore become coated with oil and are then preferentially adsorbed on the surface of the gas bubbles

and rise with them to the top of the flotation tank. The froth of bubbles spills over the top of the tank, carrying the ore particles with it. Collapse of the froth bubbles leaves a solid mass of highly concentrated ore. The impurities are not adsorbed by the gas bubbles and remain behind in the tank. As the quality of available ores decreases, more and more of them are concentrated by flotation.

3. *Leaching of the ore* with an appropriate solvent (H_2SO_4, NaCN). This method of treatment, originally used only for recovery of copper from its low-grade ores and of silver and gold from their ores, is now used for recovering a number of additional metals from their high-grade ores, among them Zn, Cd, Mn, Cr, Co, and Ni.

4. *Magnetic separation.* Low-grade *taconite* iron ores containing the magnetic oxide magnetite (Fe_3O_4) are successfully concentrated by this method. A magnet plucks the magnetite particles out of the finely pulverized ore, leaving the nonmagnetic impurities behind.

5. In nearly all high-temperature reduction by C or CO, *impurities* (sand, limestone, various other rocks, etc.) *are removed as a low-melting slag by addition of an appropriate flux.* The flux reacts with the impurity to form the slag, which in the molten condition, rises to the top of the more dense mass of liquid metal and can then be poured off or skimmed off. In the case of iron ores from the Minnesota mines, the chief impurities are sand and silicate rocks. Limestone ($CaCO_3$) is added as a flux. It reacts with the siliceous materials as follows:

$$CaCO_3 + SiO_2 = CO_2 + CaSiO_3 \text{ (slag)}$$

$$6\,CaCO_3 + 2\,KAlSi_3O_8 = \underbrace{K_2SiO_3 + 5\,CaSiO_3 + Ca(AlO_2)_2}_{\text{slag}} + 6\,CO_2$$

The process is carried out in large *blast furnaces*, and the heat required comes from the combustion of the coke which is mixed with the charge of ore and flux.

D. *Degree of Purity Required in the Metal.* If high purity is desired it can be attained by:

1. *Electrolytic refining of the crude metal* (Cu, Zn, Cr, Mn, Cd). The impure metal obtained by reduction of the ore is made the positive electrode in an electrolysis cell in which starting sheets of pure metal serve as negative electrodes (see Figure 25.3). The impure metal goes into solution:

$$Cu = Cu^{++} + 2e$$

and is then redeposited as pure metal on the starting sheet at the negative pole.

$$Cu^{++} + 2e = Cu$$

As in all electrolysis and electrodeposition processes, the metal is dissolved and electrodeposited in accordance with Faraday's law, which states that 1 faraday (96,540 coulombs) of electricity will dissolve or deposit 1 gram-equivalent weight of an element.

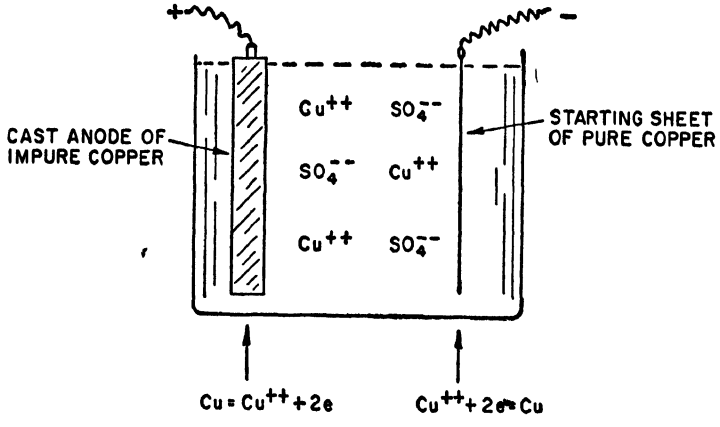


Figure 25.3. The electrolytic refining of copper.

2. *Purification of the ore prior to electrodeposition or reduction* (Cr, Mn, Al, Mg). For example, crude bauxite ore (Al_2O_3) is first digested with NaOH as a means of extracting the amphoteric aluminum oxide from the impurities.

$$2\,Na^+ + 2\,OH^- + Al_2O_3 = 2\,Na^+ + 2\,AlO_2^- + H_2O$$

Pure $Al(OH)_3$ is then precipitated by treatment of the $NaAlO_2$ solution with acid.

$$Na^+ + AlO_2^- + H_2O + H^+ = Na^+ + Al(OH)_3$$

The pure $Al(OH)_3$ is then dehydrated by heating to give pure Al_2O_3.

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

When this pure Al_2O_3 is dissolved in fused Na_3AlF_6 and electrolyzed, pure aluminum is obtained.

3. *Special processing* (Ag, Au, and some of the less common metals)

E. *Presence in the Ore of Ores of Other Recoverable Metals.* If the crude "work dirt" contains ores of similar or closely related metals (Zn and Cd; Cu and Cd; Cu and Ag; Pb and Ag) special processes, sometimes very complicated, must be employed to separate the metals. The special processes may include:

1. *Electrodeposition* (Ag and Au from Cu and from Zn). In the

purification of copper and zinc by electrorefining, the gold and silver that are present as impurities do not go into solution during the electrolysis operation but drop to the bottom of the tank as *electrolytic mud*, from which they are later removed.

2. *Replacement* (Cd from Zn). Cadmium is always present in zinc ores, and accordingly is present in the crude zinc metal. If the ore, or the crude metal, is dissolved in sulfuric acid and the resulting sulfate solution is brought in contact with zinc metal, the less electropositive cadmium will be replaced from solution by the more electropositive zinc.

$$Zn + Cd^{++} = Zn^{++} + Cd$$

The zinc can now be separated in the pure form from the cadmium-free solution by electrolysis.

3. *Extraction with a solvent* (Ag from Pb; Zn from Cd). Silver is very soluble in molten zinc, which in turn is insoluble in molten lead. Therefore if lead, which generally contains silver as impurity, is melted and then shaken with melted zinc, the zinc will dissolve the silver but will not dissolve any appreciable amount of lead. If the agitated mixture is allowed to stand, the more dense silver-free lead will settle to the bottom and the less dense zinc with its dissolved silver will rise to the top and can be skimmed off. The more volatile zinc can then be distilled off and condensed, leaving the less volatile silver behind.

25.11 United States production and consumption of the common metals. Some idea of the relative importance of the common metals is indicated by the figures given in Table 25.2. These, and all other 1950 production figures given in this book, are taken from the *Minerals Yearbook* of the U. S. Department of the Interior.

25.12 Alloys of metals. When one or more metals (or such nonmetals as silicon, carbon, and phosphorus) are dissolved in a molten metal and the product is cooled, the solid mass that is obtained is called an *alloy*. The properties of an alloy are determined by:

(1) *the properties of the component metals;* (2) *the composition.*

In general the properties of an alloy are different from the properties of each of the pure components, and these properties will vary continuously and in most cases quite uniformly with the composition. By changing the composition of the alloy one can get a product whose properties will range all the way from those of one pure metal to the other. The significant properties which vary with the composition are (a) melting point or "softening" point, (b) hardness, (c) ductility, (d) malleability, (e) tensile strength, (f) elasticity, (g) electric conductivity,

(h) color, (i) resistance to corrosion by various corroding agents, (j) coefficient of expansion. It is obvious from what has been stated above that it is possible to prepare an alloy with about any set of properties that one might desire. This feature of alloys makes them superior to the pure metal. For that reason pure metals are seldom used. The metallic structural materials are usually alloys.

TABLE 25.2

1950 U.S. PRODUCTION AND CONSUMPTION OF COMMON METALS

Metal	*Production* (tons)	*Consumption* (tons)
Iron (steel)	96,836,000	96,836,000
Copper	921,000	2,222,000
Aluminum	718,622	1,202,000
Zinc	622,000	1,149,000
Lead	419,000	1,440,000
Manganese	187,000	1,205,000
Magnesium	15,726	26,293
Cadmium	4,595	4,751
Antimony	2,497	35,517
Nickel	913	93,167
Cobalt	405	5,926
Chromium	116	282,000
Mercury	172	1,870
Tin	15	129,883
Silver	42.46 million ounces	...
Gold	2.4 million ounces	...

Some of the more important familiar alloys are:

1. *Steels.* Steel is iron alloyed with carbon alone or carbon and other metals. Since the prime requisites of steel are strength, hardness, and toughness, and since these qualities are obtained when dense atoms of small diameters crystallize in a system containing other dense atoms of small diameters, it follows that the most desirable elements to use in making alloy steels are the transition metals. The following transition metals are cheap enough and plentiful enough so that their large-scale use is practical: Cr, Mn, Ni, Co, Ti, V, Mo, W, and Ta. Copper and silicon are used in making corrosion-resistant steel.

2. *Brass.* Copper and zinc in varying amounts are the basic metals. Small amounts of other metals may be present.

3. *Bronze.* Copper and tin in varying amounts are the basic metals. Small amounts of other metals may be present.

4. *Solder.* Lead and tin in varying amounts are the basic metals. Small amounts of other metals may be present.

5. *Gold coin* is 10% Cu and 90% Au.

6. *Silver coin* is 10% Cu and 90% Ag.

7. *Sterling silver* is 7.5% Cu and 92.5% Ag.
8. *Thousands of other nonferrous alloys.*

25.13 The use of metals in batteries. When two metals (or a metal and nonmetal, or a metal and a suitable insoluble compound, or two such compounds) are placed in an electrolyte solution and are connected by a suitable conductor, electrons will flow through the conductor from the metal of higher oxidation potential to the one of lower potential. The setup is referred to as a *galvanic cell*, *voltaic cell*, or *battery*, and the combination of two metals is called a *couple*. The voltage developed by the battery is the algebraic difference between the oxidation potentials of the two parts of the couple (see 20.5).

To illustrate how a battery operates: if a zinc-hydrogen gas couple is immersed in a solution of $ZnSO_4$ and sulfuric acid in water a current will flow as a result of the following reactions.

At the zinc plate: Zinc, being more electropositive than hydrogen, goes into solution to form zinc ions according to the reaction $Zn = Zn^{++} + 2e$. These electrons are picked up by the zinc plate, which is the nearest conductor. As a result the zinc plate is referred to as the *negative pole*. The electrons travel along the external circuit to the hydrogen plate. This flow of electrons is referred to as an *electric current*. As a result of the movement of electrons, they are found on both the zinc and hydrogen plates. However, the number of electrons per unit surface on the hydrogen plate is less than the number on the zinc plate (see Figure 25.4). That means that the hydrogen plate is *less negative* than the zinc plate. It is therefore referred to as the *positive pole*.

At the hydrogen electrode: The hydrogen ions in the solution are

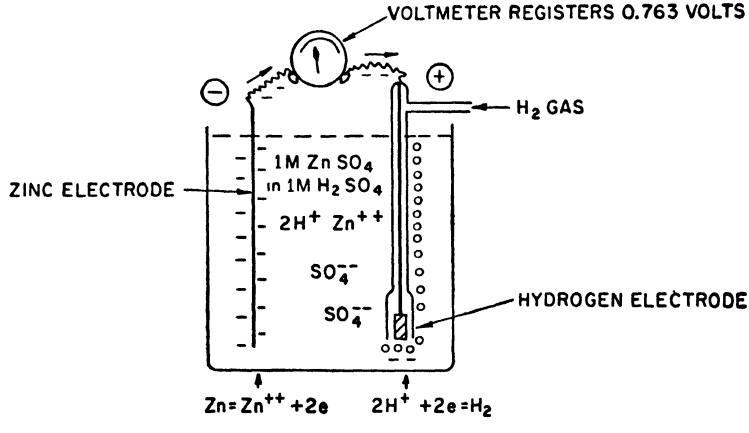


Figure 25.4. A zinc-hydrogen gas battery.

attracted by the electrons on the hydrogen plate. As a result the reaction $2\ H^+ + 2e = H_2$ takes place at that plate. This removes electrons from the hydrogen plate and thereby allows more zinc to go into solution to produce more electrons to be conducted along the external circuit.

The oxidation potential ($E°$) of the half reaction $Zn = Zn^{++} + 2e$ is 0.763 volt (see Table 20.1 or 25.1), while the potential of the reaction $2\ H^+ + 2e = H_2$ is 0.00 volt. The theoretical voltage of the battery is therefore 0.763.

A similar combination of half reactions occurs whenever a couple is formed. The metal of higher oxidation potential is always the negative pole. The greater the difference in their potentials, the higher the voltage of the battery.

The following are important industrial batteries:

1. *The Daniell cell* (see Figure 25.5). This consists of a zinc plate immersed in a solution of $ZnSO_4$ and a copper plate immersed in a solution of $CuSO_4$. The two solutions are in contact with each other. The

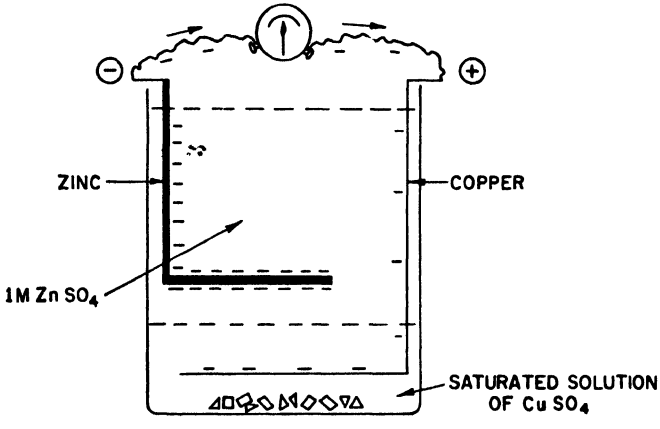


Figure 25.5. The Daniell cell.

zinc plate is the negative pole, the reaction being $Zn = Zn^{++} + 2e$. The reaction at the copper plate is $Cu^{++} + 2e = Cu$. Since the potentials ($E°$) of the two reactions are, respectively, 0.763 and -0.337, the theoretical voltage of the battery is 1.1.

2. *The dry battery* (see Figure 25.6). A graphite electrode is immersed in a paste made up of water, NH_4Cl, and MnO_2 contained in a zinc can. The following reactions take place.

$Zn = Zn^{++} + 2e$ (the zinc container becomes the negative pole)

$2\ NH_4^+ + MnO_2 + 2e = 2\ NH_3 + MnO + H_2O$

The voltage of the cell is about 1.5. It should be noted that the dry battery is not actually dry. It is one of the most useful, convenient, and widely used batteries. Millions of individual units are manufactured each year for use in flashlights and other devices.

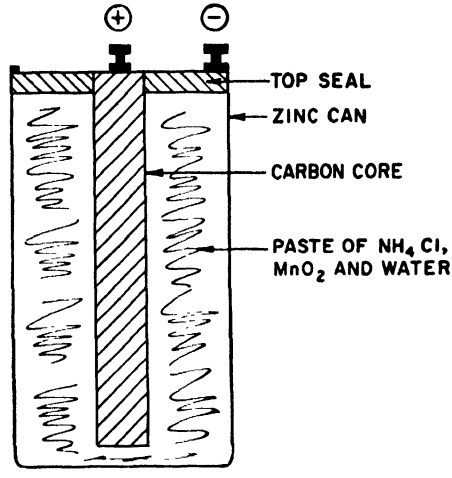


Figure 25.6. The dry battery.

3. *The lead storage battery* (see Figure 25.7). The negative plate consists of spongy lead supported on a grid made from a lead-antimony or lead-arsenic alloy. The positive pole is spongy PbO_2 supported in a similar grid. The electrolyte is sulfuric acid. The discharge reactions that take place when the battery delivers current are:

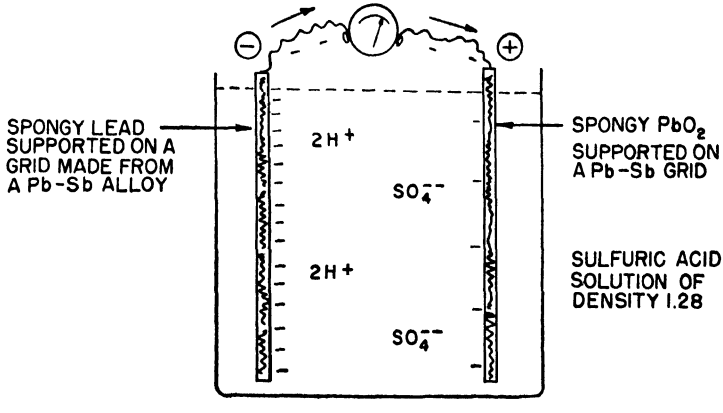


Figure 25.7. A single-unit lead storage battery.

At the lead plate:

$$Pb + SO_4^{--} = PbSO_4 + 2e$$

At the PbO_2 plate:

$$PbO_2 + SO_4^{--} + 4\,H^+ + 2e = PbSO_4 + 2\,H_2O$$

The voltage of the battery is about 2.0. As a result of the reactions that occur, sulfuric acid is used up, water is produced, and both plates are converted to $PbSO_4$. Because the density of water is about 1, while that of pure H_2SO_4 is about 1.85, the density of the electrolyte decreases as a result of the delivery of current. For that reason one can determine the extent to which the battery has "run down" by measuring the density (or specific gravity) of the acid.

A storage battery can be recharged by attaching the lead plate to the negative pole and the PbO_2 plate to the positive pole of a d-c circuit and allowing electricity to flow through. The following reactions will take place:

At the lead plate:

$$PbSO_4 + 2e = Pb + SO_4^{--} \qquad E^\circ = 0.356 \text{ volts}$$

At the PbO_2 plate:

$$PbSO_4 + 2\,H_2O = SO_4^{--} + 4\,H^+ + PbO_2 + 2e \qquad E^\circ = -1.685 \text{ volts}$$

These charging reactions are the exact reverse of the discharge reactions. As a result, the $PbSO_4$ and H_2O are converted back to Pb, PbO_2, SO_4^{--} ions and H^+ ions.

Theoretically, a lead storage battery should last indefinitely. Failure to achieve this long life is largely the result of mechanical and structural breakdown (cracking the shell of the battery and allowing the acid to leak out, breakdown of the insulation between the Pb and PbO_2 plates with resultant development of short circuits, use of water containing iron salts with resultant oxidation and reduction of Fe^{++} and Fe^{+++}, disintegration of the plates by the vibration of the car, drying up of plates due to leak of water, and excessive precipitation of $PbSO_4$ resulting from failure to keep the battery fully charged). Millions of storage batteries are in use in automobiles, trucks, tractors, and other installations. About 150,000 tons of lead are used annually in the United States for the manufacture of these batteries.

4. *The Edison cell.* The negative pole is a sheet of pure iron. The positive pole is NiO_2. The electrolyte is a solution of KOH. The discharge reactions are:

At the iron plate:

$$Fe + 2\,OH^- = Fe(OH)_2 + 2e \qquad E^\circ = 0.877 \text{ volts}$$

At the NiO_2 plate:

$$NiO_2 + 2\,H_2O + 2e = Ni(OH)_2 + 2\,OH^- \qquad E^\circ = -0.49 \text{ volts}$$

These reactions are reversed and the battery is recharged when direct current is passed through the cell with the negative pole of the generator attached to the iron plate.

The Edison cell has a voltage of about 1.3. By comparison with the lead storage cell it is bulkier and more expensive, but its in-service life is longer because of its ruggedness and resistance to mechanical breakdown.

Questions

1. Define or describe and illustrate each of the following: light metal; heavy metal; noble metal; base metal; alkali metal; alkaline earth metal; metalloid; transition element; ductility; malleability; electropositivity; oxidation potential; metal bonding; cation; salt; coordination number; ore; metallurgy; flotation; roasting; alloy; galvanic cell; voltaic cell.

2. Enumerate the physical properties which characterize the metals. Account for these properties in terms of the electronic configuration of the atom of the metal.

3. Enumerate the chemical properties which characterize the metals.

4. Where do the metals fall in the periodic table? The transition metals? The metalloids? The alkali metals? The alkaline earth metals? The most reactive metals? The light metals? The dense metals? The softer metals? The harder metals? The metals that are used in making alloy steels? The metals of larger atomic diameters? The metals of smaller atomic diameters?

5. How do the metallic character of an element and the basic character of its hydroxide vary with: (a) its position in a given periodic group? (b) its position in a given periodic period?

6. Enumerate the unique properties of the transition elements and their ions and compounds.

7. Enumerate eight methods that can be used for preparing salts.

8. Point out the relation between the position of a metal in the

electropositivity table and the chemical form in which it occurs in its ores.

9. What factors determine the metallurgical process that is followed in obtaining a metal from its ore?

10. What determines the properties of an alloy? What properties of an alloy are of particular importance and significance in connection with its commercial use? Why have alloys largely taken the place of the pure metals in industry?

11. What metals are used in preparing the following alloys? Steel, solder, bronze, sterling silver, brass, silver coin, gold coin.

12. Describe the operation of each of the following batteries: (a) dry battery; (b) Daniell cell; (c) lead storage battery; (d) Edison cell. In (c) and (d) indicate what takes place when the battery is recharged.

13. List the six top metals from the standpoint of annual U.S. production.

CHAPTER 26

Gold, Silver, Mercury, Copper

26.1 The elements of group IB, and mercury. Because gold, silver, mercury, and copper are of such low reactivity, they occur free in nature. For that reason they were the first metals used extensively by man; long before he learned the art of converting iron ore into iron for use in making swords and spears, gold, silver, and copper were among his prized possessions.

Although mercury falls in group IIB along with zinc and cadmium it actually is more like the members of group IB, and will accordingly be discussed with them.

The significant physical and atomic properties of the four elements are given in Table 26.1. They are all dense metals of relatively small atomic diameters and high electric and thermal conductivity.

Their oxides are weakly basic, CuO being the most strongly basic of the four; Au_2O_3 is actually acidic in character. The principal oxidation state of copper and mercury is 2, of gold and silver is 1.

Gold

26.2 Production in ounces (1950): (These and all other production figures for the metals refer to *primary production*, that is, to production from ores. They do not include *secondary production*, that is, metal recovered from scrap metal and scrap alloys, unless specifically indicated.) World, 31,600,000; U.S., 2,394,231 (S. Dak., 567,996; Utah, 457,551; Calif., 412,118; Alaska, 289,272; Nev., 178,447; Colo., 130,380; Ariz., 118,313). 1952 U.S. production, about 1,885,000. It is of interest to note that the total value of all recorded gold produced in the world up through 1952 is about $42,723,000,000.

26.3 Occurrence. It occurs chiefly as metallic gold and the telluride, $AgAuTe_2$.

26.4 Metallurgy. The following metallurgical processes are employed:

A. *Placer Mining.* A stream of water under pressure, directed at the gold-bearing sand, carries the sand and gold into sluices. The heavier

TABLE 26.1

PHYSICAL PROPERTIES OF COPPER, SILVER, GOLD, AND MERCURY

Element	Period	At. no.	At. wt	At. diam, Å	Configuration	Density g/cc	Mp °C	Bp °C	Color and state	Conductivity	Oxidation states
Copper	4	29	63.54	2.56	2, 8, 18, 1	8.92	1084	2595	red, solid	excellent	1, 2
Silver	5	47	107.88	2.88	2, 8, 18, 18, 1	10.5	961	2212	silver-gray, solid	best	1
Gold	6	79	197.2	2.88	2, 8, 18, 32, 18, 1	19.3	1063	2966	yellow, solid	excellent	1, 3
Mercury	6	80	200.61	3.14	2, 8, 18, 32, 18, 2	13.55	−38.9	357	silver-white, liquid	excellent	1, 2

gold sinks to the bottom of the suspension and is caught in depressions in the sluice, while the sand and dirt are carried away. About 27% of the annual U.S. production is by this method.

B. *Vein Mining.* About 45% of the average annual U.S. production is by this mining process. The gold-bearing rock is mined, then crushed, and the gold is extracted from the pulverized mass by one of the following methods:

1. *Amalgamation with mercury.* The finely pulverized mixture of rock and gold is agitated with water and the suspension is allowed to flow through sluices whose bottoms are covered with mercury. The heavy gold particles settle onto the mercury and are dissolved (amalgamated) by it. The gold-bearing mercury is placed in stills and the mercury, which boils at 357°C, is distilled off and recovered by condensation for reuse. The gold, which boils at 2966°C, remains behind in the still. About 23% of the gold produced in the U.S. is extracted by amalgamation.

2. *Leaching with* NaCN *solution.* The pulverized mass is placed in a solution of NaCN and the mixture is well aerated by thorough agitation. After filtration or gravity settling, the gold is recovered from the resulting solution by electrodeposition or replacement by Zn. About 15% of the annual U.S. production is by this process. The following detailed reactions take place:

$$4\,Au + 8\,CN^- + 2\,H_2O + O_2\ (\text{from air}) = 4\,OH^- + 4\,Au(CN)_2^-$$

$$Au(CN)_2^- \rightleftarrows Au^+ + 2\,CN^-; \qquad Au^+ + e = Au$$

$$Zn + 2\,Au^+ = Zn^{++} + 2\,Au$$

C. *Smelting.* The gold-bearing rock is heated and the dense molten gold sinks to the bottom of the furnace and is drawn off. This, obviously, is used only on rock of high gold content. About 8% of the U.S. annual gold production is a *by-product* in the smelting of copper, lead, and zinc ores.

D. *Refining.* The crude gold that is recovered by the methods outlined above generally contains other metals as impurities. It can be separated from these metals by:

1. *Electrolysis.* The impure gold is dissolved in NaCN solution, which is then electrolyzed to yield pure gold at the negative electrode.

2. *Cupellation.* The impure gold is heated in air on a bone ash [$Ca_3(PO_4)_2$] hearth. The Cu, Pb, Zn, and other reactive metals are oxidized, and the oxides are absorbed by the bone ash, leaving pure gold.

3. *Parting with* H_2SO_4. All metals except gold are dissolved away by treatment with hot concentrated sulfuric acid.

26.5 Properties (see Table 26.1). Gold is a noble metal, very ductile and malleable; it is very inactive, dissolving slowly in aqua regia.

$$Au + 4\,Cl^- + NO_3^- + 4\,H^+ = AuCl_4^- + NO + 2\,H_2O$$

26.6 Uses. It is used as a reserve by the U.S. Treasury, for jewelry, and for ornamental gold leaf. Its purity or "fineness" is expressed in carats; pure gold is 24 carat. Ten carat gold contains 10 parts by weight of gold and 14 parts by weight of alloying metals (usually copper). Fourteen carat gold contains $\frac{14}{24} \times 100\%$, or about 58% by weight of gold. It should be noted that the carat has an entirely different value when applied to diamonds than when applied to gold. The carat, as applied to diamonds, is a unit of mass, and as such gives the *weight* of the pure diamond; it does not denote the purity of the diamond. One carat is equivalent to about 0.2 g; a 10-carat diamond would weigh 2 g. The word "carat" comes from a Greek word which refers to the bean of the *carob*, or locust, tree. These beans were long ago used as the unit of mass when weighing diamonds. The unit has changed but the name, carat, is still used.

Silver

26.7 Production, in ounces (1950): World, 192,000,000; Mexico, 49,141,000; U.S., 42,460,000 (Idaho, 16,095,000; Utah, 7,084,000; Mont., 6,591,000; Ariz., 5,325,000; Colo., 3,492,000); Canada, 22,386,000; Peru, 19,141,000. 1952 U.S. production, about 39,000,000.

26.8 Occurrence. Silver occurs as free silver, argentite, Ag_2S, and argyrite, AgCl.

26.9 Metallurgy. About 76% of the annual U.S. production is a by-product in the metallurgy of Cu, Pb, Zn, and Cd, only 24% being the result of processes in which the silver is the primary desired product. About 98% of the U.S. production is by involved processes which include roasting and smelting followed by electrodeposition and/or extraction with zinc and/or extraction with acid and/or cupellation. The roasting in air followed by reduction with coke yields an alloy containing silver along with one or more of the following: Au, Cu, Pb, Zn, Cd. If silver is the primary metal, the others being present as impurities, the base metal impurities are first removed by cupellation as described under gold. The silver can be separated from the gold by treatment with concentrated H_2SO_4 and can be recovered from the resulting solution by electrolysis. If silver is the impurity it can be extracted (from Pb) by

agitation of the molten mass with molten zinc or by electrolysis. In the former process the zinc is then distilled off, leaving the less volatile silver behind; in the latter process the silver, along with the gold, settles to the bottom of the electrolysis tank and is later purified by cupellation and parting. About 2% of our annual production of silver is obtained by cyanide extraction followed by zinc replacement or electrolysis. The following reactions occur:

$$4\,Ag + O_2 \text{ (from air)} + 8\,CN^- + 2\,H_2O = 4\,Ag(CN)_2^- + 4\,OH^-$$
$$Ag_2S + 4\,CN^- = 2\,Ag(CN)_2^- + S^{--}$$
$$AgCl + 2\,CN^- = Ag(CN)_2^- + Cl^-$$
$$Zn + 2\,Ag(CN)_2^- = 2\,Ag + Zn(CN)_4^{--}$$
$$Ag(CN)_2^- \rightleftarrows Ag^+ + 2\,CN^-$$
$$Ag^+ + e = Ag$$

26.10 Properties. Silver is a noble metal; it has an attractive silver-white color, and is the best known conductor of heat and electricity (see Table 26.1).

26.11 Uses of the metal. It is used for coin (90% Ag, 10% Cu), sterling silver (92.5% Ag, 7.5% Cu), jewelry, plating, mirrors, manufacture of $AgNO_3$ and silver halides, and dental amalgam. (Dental amalgam is an alloy of silver and mercury.)

26.12 Important commercial compounds and their uses

1. $AgNO_3$. It is used for the manufacture of AgBr, AgI, AgCl, and other silver compounds, silvering mirrors, cauterization, marking inks, analytical reagent. Every metal has a main compound which is used as the starting point in the preparation of other compounds. In the case of silver this compound is $AgNO_3$. It is prepared by dissolving pure silver in nitric acid.

2. The halides AgBr, AgI, AgCl are used for the manufacture of photographic film. About 18% of our annual production of silver is consumed in producing photographic film.

3. The salt $NaAg(CN)_2$ serves as the electrolyte in silver-plating baths. The article to be plated is attached to the negative electrode, while the positive electrode is a slab of pure silver. The electrolyte $NaAg(CN)_2$ ionizes to give Na^+ and $Ag(CN)_2^-$ ions. The $Ag(CN)_2^-$ ion ionizes to give Ag^+ and 2 CN^- ions. The reactions that take place during electrodeposition are:

At the positive electrode: $Ag = Ag^+ + e$
At the negative electrode: $Ag^+ + e = Ag$

26.13 Reactions

1. The half-cell reaction, $Ag = Ag^+ + e$; $E^\circ = -0.7991$. The low voltage shows that silver is weakly electropositive and relatively inactive. It accounts for the fact that silver will not replace hydrogen from dilute acids and will be replaced from a solution of its ions by all metals in the reactivity table (Table 25.1) except Pt and Au.

2. Reaction of Ag with concentrated HNO_3, to yield $AgNO_3$ solution. This is the commercial method for preparing $AgNO_3$.

$$Ag + NO_3^- + 2\,H^+ = Ag^+ + NO_2 + H_2O$$

3. Reaction of Ag with sulfur and sulfur compounds. These reactions are responsible for the tarnishing of silverware by formation of black Ag_2S.

$$2\,Ag + S = Ag_2S \text{ (black)}$$
$$4\,Ag + 2\,H_2S + O_2 \text{ (from air)} = 2\,Ag_2S + 2\,H_2O$$
$$4\,Ag + 2\,S^{--} \text{ (soluble sulfides)} + O_2 + 2\,H_2O = 2\,Ag_2S + 4\,OH^-$$

4. Thermal decomposition of Ag_2O. This is a laboratory source of oxygen.

$$2\,Ag_2O \text{ (heated)} = 4\,Ag + O_2$$

5. Reaction of AgCl with NH_4OH to form the soluble complex diammine ion $Ag(NH_3)_2^+$. This reaction is the basis, in most plans of qualitative analysis, for the separation of silver from mercury(I).

$$AgCl + 2\,NH_4OH = Ag(NH_3)_2^+ + Cl^- + 2\,H_2O$$

The $Ag(NH_3)_2^+$ ion is converted back to AgCl when the solution is acidified with HNO_3. This is the basis for the identification of silver in most qualitative analytical procedures.

$$Ag(NH_3)_2^+ + Cl^- + 2\,H^+ = AgCl + 2\,NH_4^+$$

6. Reaction of silver ions with various anions to form characteristically colored precipitates. These reactions are the basis for use of a silver nitrate solution for detection of the anions in qualitative analysis. If addition of $AgNO_3$ solution to an unknown solution yields one of the characteristically colored precipitates formed in the following reactions, the presence of the particular anion responsible for the formation of that precipitate is indicated.

$$\begin{aligned} Ag^+ + \begin{cases} Cl^- & = AgCl \text{ (white)} \\ Br^- & = AgBr \text{ (cream colored)} \\ I^- & = AgI \text{ (pale yellow)} \\ S^{--} & = Ag_2S \text{ (black)} \\ SO_3^{--} & = Ag_2SO_3 \text{ (white)} \\ CO_3^{--} & = Ag_2CO_3 \text{ (white)} \\ BO_2^- & = AgBO_2 \text{ (white)} \\ CrO_4^{--} & = Ag_2CrO_4 \text{ (red)} \\ PO_4^{---} & = Ag_3PO_4 \text{ (yellow)} \\ AsO_4^{---} & = Ag_3AsO_4 \text{ (chocolate brown)} \end{cases} \end{aligned}$$

The precipitates of AgCl, AgBr, AgI, and Ag_2S formed in the above reactions are insoluble in dilute HNO_3; the other six precipitates are readily dissolved by dilute HNO_3 according to the following reactions:

$$\begin{aligned} Ag_2SO_3 + H^+ \text{ (from } HNO_3) &= 2\,Ag^+ + H_2SO_3 \\ Ag_2CO_3 + H^+ \text{ (from } HNO_3) &= 2\,Ag^+ + H_2O + CO_2 \\ AgBO_2 + H^+ \text{ (from } HNO_3) &= Ag^+ + HBO_2 \\ 2\,Ag_2CrO_4 + H^+ \text{ (from } HNO_3) &= 4\,Ag^+ + H_2Cr_2O_7 \\ Ag_3PO_4 + H^+ \text{ (from } HNO_3) &= 3\,Ag^+ + H_3PO_4 \\ Ag_3AsO_4 + H^+ \text{ (from } HNO_3) &= 3\,Ag^+ + H_3AsO_4 \end{aligned}$$

The solubility of these six precipitates illustrates the fact that the water-insoluble salt of a *weak acid* is as a general rule soluble in a strong acid. The fact that AgCl, AgBr, and AgI are insoluble in dilute HNO_3 illustrates the rule that the water-insoluble salt of a *strong acid* is insoluble in a strong acid.

7. Reaction of silver ions with a solution of an alkali. This is a commercial method for preparing Ag_2O. Silver hydroxide is even more unstable toward heat than its oxide. As a result, Ag_2O is formed when Ag^+ and OH^- ions react at room temperature.

$$Ag^+ + OH^- = \mathbf{AgOH}; \qquad 2\,AgOH = Ag_2O + H_2O$$

8. Oxidation by silver nitrate. This is the basis for the use of dilute silver nitrate solutions as a disinfectant in medicine, particularly for cauterizing the eyes of all new-born babies. It represents likewise what takes place when a more concentrated $AgNO_3$ solution is used as an ink for marking fabrics.

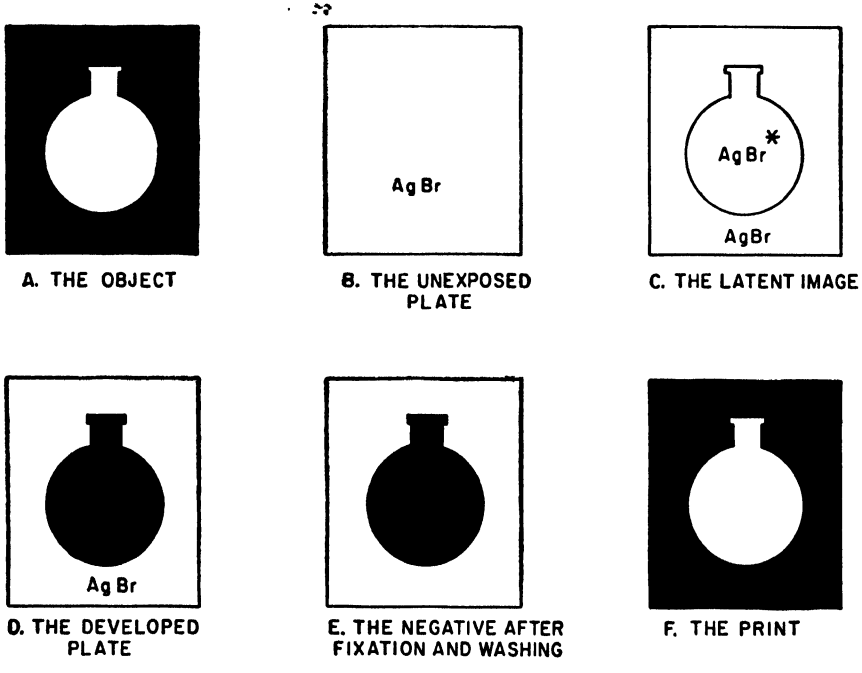
$$Ag^+ + \text{oxidizable material } (e) = Ag + \text{oxidized product}$$

9. Manufacture of silver mirrors. Clean plate glass is brought in contact, for several minutes, with a solution in which the reaction given below takes place. The silver that is formed deposits as a shiny film on the surface of the glass. A number of reducing agents can be used in place of formaldehyde (HCHO).

$$2\,Ag(NH_3)_2^+ + HCHO + 2\,H_2O = 2\,Ag + NH_4OH + 3\,NH_4^+ + HCOO^- \text{ (formate ion)}$$

10. *Reactions in the simple photographic process.* The original unexposed plate (Figure 26.1B) consists of a colloidal suspension of AgBr in gelatin spread, in the form of a thin film, on a sheet of glass or transparent plastic. The four steps in the photographic process are:

Exposure. If the camera is properly focused, an inverted image of the object (see Figure 26.1A) to be photographed is caused, by the lens or pinhole, to fall upon the plate when the shutter is opened. The image is formed because light is reflected from the object; the whiter the object the greater the amount of light reflected. Light converts normal AgBr to an active, sensitive form. Since the amount of active AgBr formed is proportional to the light that falls on the plate this active AgBr produces what is referred to as an invisible *latent image* on the exposed film



A. THE OBJECT
B. THE UNEXPOSED PLATE
C. THE LATENT IMAGE
D. THE DEVELOPED PLATE
E. THE NEGATIVE AFTER FIXATION AND WASHING
F. THE PRINT

Figure 26.1. Steps in the photographic process.

(see Figure 26.1C). The reaction that takes place on exposure is

$$\text{AgBr} + \text{light} = \text{active AgBr}^*$$

Development. The active AgBr is much more easily reduced to Ag than is the normal AgBr. Therefore if the exposed film is placed for the correct length of time in a reducing solution of the correct strength, the active AgBr is reduced to Ag but the normal AgBr is not affected (see Figure 26.1D). The development reaction may be represented as

$$\text{AgBr}^* + \text{reducing agent } (e^-) = \text{Ag} + \text{Br}^-$$

Fixation. Having reduced the active AgBr to Ag, the normal AgBr still left on the plate must be removed. This is done by dissolving it in *hypo* (sodium thiosulfate, $Na_2S_2O_3$).

$$\text{AgBr} + 2\,S_2O_3^{--} = Ag(S_2O_3)_2^{---} + \text{Br}^-$$

After treatment with hypo the plate is washed and dried. The plate at this stage is called the *negative* because it is the reverse of the original object; the light-colored parts of the object are dark on the negative, and vice versa (see Figure 26.1E).

Preparation of the print. This involves repetition of the three steps given above except that the plate is replaced by a piece of print paper impregnated with AgBr. The negative is placed on top of this print paper and light is allowed to fall on it for a definite length of time. The amount of light that strikes the print paper, and hence the amount of active AgBr formed, will be proportional to the light that passes through the negative. As a result, when the exposed piece of print paper is finally developed, fixed, and washed the picture will be the reverse of the negative and the same as the original object (see Figure 26.1F).

Mercury

26.14 Mine production in tons (1950). (*Mine production* means the quantity of primary metal obtained from ores mined in the particular country. It does not include primary metal produced from ores that are imported from other countries.) World, 5170; Italy, 2030; Spain, 1900; U.S., 172; Mexico, 141. U.S. consumption, 1870; 1952 U.S. mine production, 847.

26.15 Occurrence. Mercury occurs largely as cinnabar, HgS, and in small amount as free Hg.

26.16 Metallurgy. Cinnabar is roasted in air. The mercury that is liberated is distilled off and condensed.

$$HgS + O_2 = Hg + SO_2$$

26.17 Properties (see Table 26.1). Mercury is a noble metal, a liquid with a high coefficient of expansion (relatively large increase in volume per degree rise in temperature), does not wet glass, mp −39°C, bp 357°C, density 13.55, excellent conductor, and its incandescent vapors are rich in ultraviolet light.

26.18 Uses. It is used in electrical apparatus including fluorescent light tubes, control instruments including thermometers, manufacture of insecticides, pharmaceuticals, antifouling paints, mercury fulminate, electrolytic cells, and dental amalgams. These uses utilize its excellent electric and heat conductivity, high coefficient of expansion, low freezing point, comparatively high boiling point, high density, fluidity (liquid state), failure to wet glass, ability to dissolve most metals, and the richness of its incandescent vapors in ultraviolet light.

26.19 Important commercial compounds and their uses

1. $Hg(CNO)_2$, mercury fulminate; detonator for initiating the explosion of smokeless powder and various high explosives (TNT, dynamite). The $Hg(CNO)_2$ is very unstable and can be exploded by shock. Its explosion causes the main explosive to be detonated.
2. $KHgI_3$; antiseptic solutions.
3. $HgCl_2$, corrosive sublimate; antiseptic solutions.
4. HgS, vermilion; red paint pigment.
5. Mercurochrome, merthiolate, mercressin, and other organic mercury compounds used as antiseptics.

26.20 Reactions

1. $2\,Hg = Hg_2^{++} + 2e$; $E^\circ = -0.789$ volt

Mercury is weakly electropositive and relatively inactive.

2. Dissolving mercury in concentrated HNO_3. This is the initial reaction in the commercial preparation of mercury compounds.

$$Hg + 2\,NO_3^- + 4\,H^+ = Hg^{++} + 2\,NO_2 + 2\,H_2O$$

3. Dissolving mercury in aqua regia.

$$3\,Hg + 2\,NO_3^- + 12\,Cl^- + 8\,H^+ = 3\,HgCl_4^{--} + 2\,NO + 4\,H_2O$$

4. Thermal decomposition of HgO. This is a laboratory source of oxygen.

$$2\,HgO = 2\,Hg + O_2$$

5. Precipitation of mercury(I) chloride. Mercury forms compounds in which its oxidation states are +1 and +2. Whereas $HgCl_2$ is moderately soluble in water, Hg_2Cl_2 is practically insoluble. The precipitation of Hg_2Cl_2 is the initial reaction in the separation and detection of mercury(I) ions in most methods of qualitative analysis.

$$2\,Hg^{+} + 2\,Cl^{-} = \mathbf{Hg_2Cl_2}\ (\text{white})$$

6. Reaction of Hg_2Cl_2 with NH_4OH. This is the reaction in qualitative analysis by which mercury(I) can be identified.

$$\mathbf{Hg_2Cl_2} + 2\,NH_4OH = \mathbf{Hg}\ (\text{black}) + \mathbf{HgNH_2Cl}\ (\text{white}) + NH_4^{+} + Cl^{-} + 2\,H_2O$$

7. Precipitation of HgS. This reaction is usually used in qualitative analysis for separation and identification of Hg^{++} ions.

$$Hg^{++} + H_2S = \mathbf{HgS}\ (\text{black}) + 2\,H^{+}$$

8. Dissolving of HgS by aqua regia

$$3\,HgS + 2\,NO_3^{-} + 12\,Cl^{-} + 8\,H^{+} = 3\,HgCl_4^{--} + 2\,NO + 3\,S + 4\,H_2O$$

9. Reduction of Hg(II) by Sn(II). Mercuric (Hg^{++}) ions are strong oxidizing agents, while Sn^{++} ions are strong reducing agents. These reactions can be used for identification of mercury(II) and tin(II) ions.

$$2\,Hg^{++}\ (\text{excess}) + Sn^{++} + 2\,Cl^{-} = \mathbf{Hg_2Cl_2} + Sn^{+4}$$
$$Hg^{++} + Sn^{++}\ (\text{excess}) = \mathbf{Hg} + Sn^{+4}$$
$$\mathbf{Hg_2Cl_2} + Sn^{++}\ (\text{excess}) = 2\,\mathbf{Hg} + Sn^{+4} + 2\,Cl^{-}$$

Copper

26.21 Mine production in tons (1950): World, 2,990,000; U.S., 921,000; (Arizona, 403,301; Utah, 278,630; New Mexico, 66,300; Montana, 54,478; Nevada, 52,569; Michigan, 25,608.) Chile, 386,000; Northern Rhodesia, 327,000; Canada, 262,000; U.S.S.R., 262,000; Belgian Congo, 197,000; Japan, 93,000; Mexico, 56,200. U.S. imports, 690,200; U.S. consumption, 2,222,000; U.S. 1952 total production 1,175,000 (920,000 from domestic ores, 255,000 from imported ores). (The fact that the total consumption of a metal in a year is greater than the sum of imports and domestic production means that we dipped into the stock pile or reserve that had accumulated from previous years' overproduction. When we consume less than the sum of what we produce and import, our reserve will increase.)

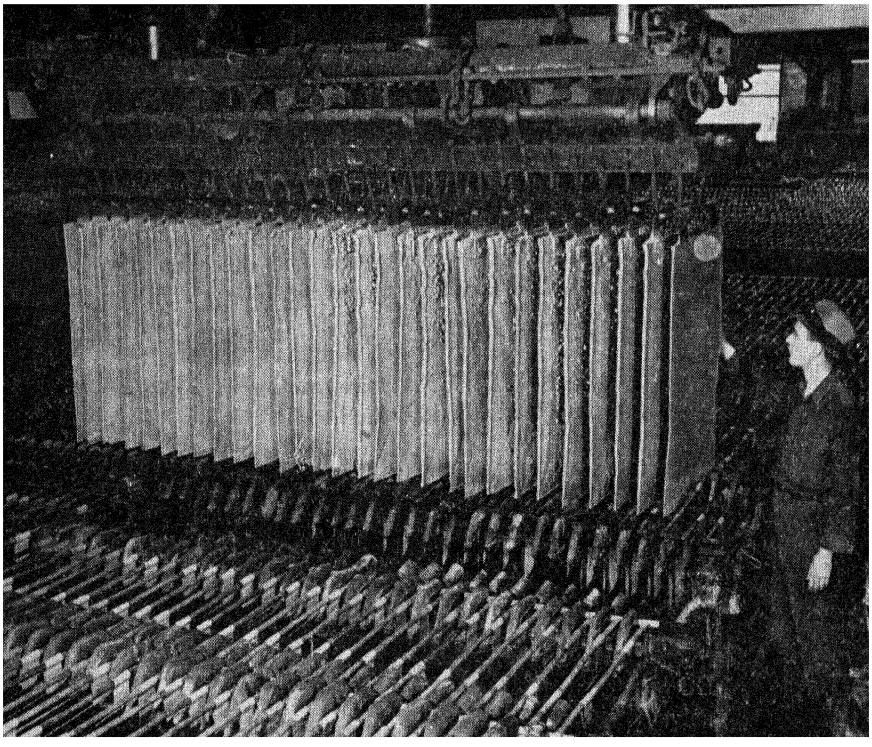


Figure 26.2. The electrolytic refining of copper. Slabs of pure copper being hoisted from the electrolytic tank. When originally placed in the tank these slabs were thin starting sheets of pure copper. After washing to remove any adhering electrolyte the slabs will be melted and cast into bars, billets and cakes. (*Courtesy Anaconda Copper Mining Company*)

26.22 Occurrence. Copper occurs as native Cu, chalcopyrite, $CuFeS_2$, chalcocite, Cu_2S, cuprite, Cu_2O, malachite, $CuCO_3 \cdot Cu(OH)_2$, and other minerals.

26.23 Metallurgy. This is a complex procedure involving (1) concentration by flotation, (2) roasting (smelting) to give a copper-enriched product called copper matte, (3) reduction by excess sulfide in the presence of sand (SiO_2) to give 98% pure "blister" copper, (4) electrolytic refining of blister copper to give pure copper (see Figures 26.2 and 26.3). The reactions that take place in (2) and (3) are

$$CuFeS_2 + O_2 + SiO_2 = CuS + SO_2 + FeSiO_3$$
$$2\,CuS + 3\,O_2 = 2\,CuO + 2\,SO_2$$
$$2\,CuO + CuS = 3\,Cu + SO_2$$

26.24 Important properties (see 26.1). Copper is characterized by the following properties: attractive color; ductile; malleable; excellent

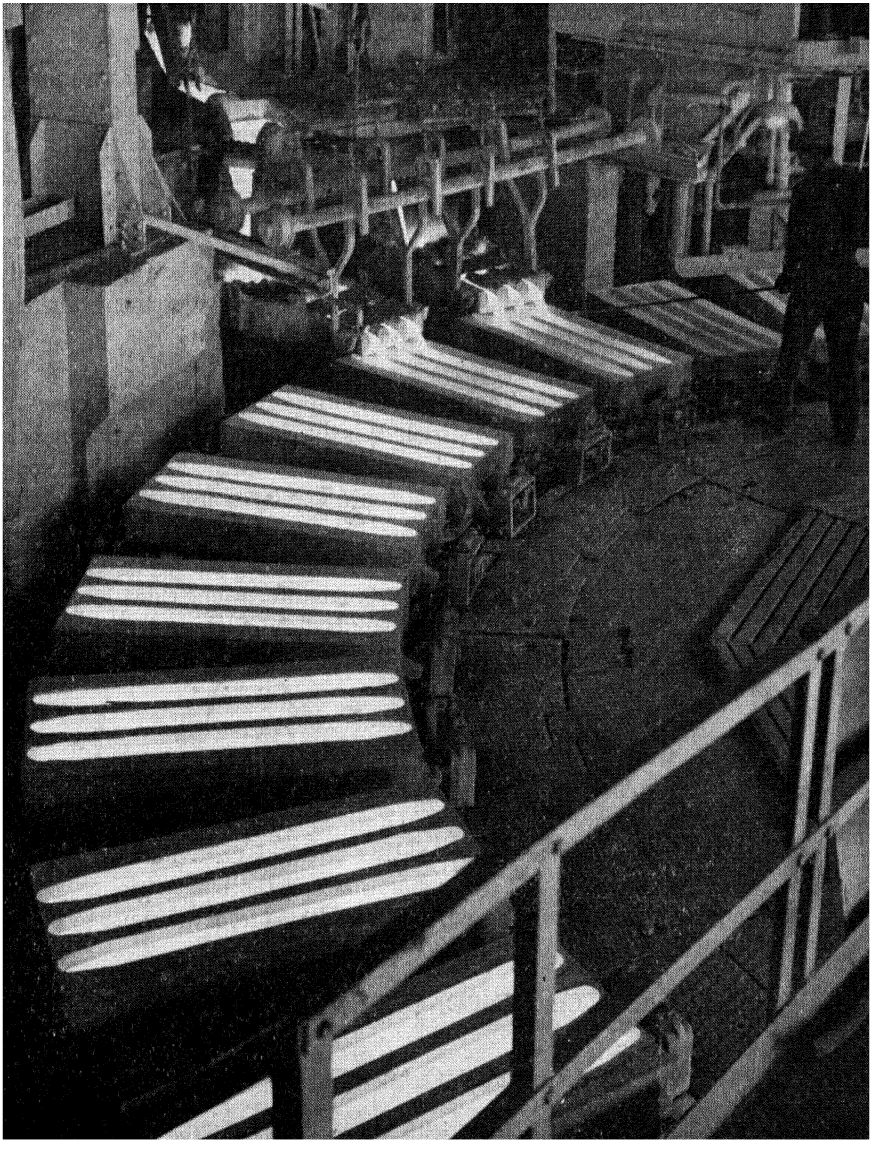


Figure 26.3. Casting pure electrolytic copper into bars. These bars may be drawn into wire of all sizes or they may be used for the preparation of numerous copper-bearing alloys. Larger bars, billets and cakes are used for the preparation of sheets, rods and tubes. (*Courtesy Anaconda Copper Mining Company*)

conductor of electricity; resists corrosion; principal oxidation state of +2 and also a stable oxidation state of +1.

26.25 Uses. The most important uses of copper are: wire for electric conductors and sheet, plates, rods, and tubes for a variety of uses (57% of total consumption); manufacture of brass, bronze, and other alloys (40% of total consumption); manufacture of copper compounds. These uses of copper are dependent upon its excellent electric conductivity, ductility, malleability, and resistance to corrosion. Brass (a copper-zinc alloy) and bronze (a copper-tin alloy) are widely used in making machine parts, castings, and pieces of equipment where resistance to tarnish and corrosion is desired.

26.26 Important commercial compounds and their uses

1. $CuSO_4 \cdot 5H_2O$, blue vitriol. It is the electrolyte in plating and electrolytic refining baths and is used for the manufacture of other copper compounds and for water treatment. The latter use depends upon the fungicidal action of copper ions.
2. $CuCO_3 \cdot Cu(OH)_2$, a fungicide
3. $Cu(OH)_2 + CaSO_4$, Bordeaux mixture, a fungicide
4. Cu_2O. It is used in the manufacture of photoelectric cells and certain kinds of batteries.

26.27 Reactions (see 26.23)

1. $Cu = Cu^{++} + 2e$; $E^\circ = -0.337$ volt
2. Leaching of low-grade ores with dilute sulfuric acid. This is an important source of $CuSO_4 \cdot 5H_2O$, which is the chief copper compound, and of copper. When $CuSO_4 \cdot 5H_2O$ is the desired product, the leach liquor is concentrated by evaporation and the blue vitriol crystallizes out. When copper is wanted, it is precipitated from the liquor by contact with scrap iron.

$$CuFeS_2\ (Cu_2S,\ Cu_2O,\ CuCO_3 \cdot Cu(OH)_2) + 4\,H^+ + SO_4^{--} + 5\,H_2O = CuSO_4 \cdot 5H_2O + Fe^{++} + 2\,H_2S$$

$$Fe + Cu^{++} = Fe^{++} + Cu$$

3. Reaction of copper with dilute H_2SO_4 in the presence of air. This is a commercial source of the chief compound, $CuSO_4 \cdot 5H_2O$.

$$2\,Cu + O_2\ (air) + 4\,H^+ + 2\,SO_4^{--} + 8\,H_2O = 2\,CuSO_4 \cdot 5H_2O$$

4. Oxidation of copper by concentrated H_2SO_4. This is a commercial source of $CuSO_4 \cdot 5H_2O$ and a laboratory source of SO_2.

$$Cu + SO_4^{--} + 4\,H^+ = Cu^{++} + SO_2 + 2\,H_2O$$

5. Oxidation of copper by HNO_3. This is a laboratory source of NO and NO_2 and a means of dissolving copper or a copper-bearing alloy.

$$3\,Cu + 2\,NO_3^- + 8\,H^+ = 3\,Cu^{++}\text{ (pale blue)} + 2\,NO + 4\,H_2O$$

$$Cu + 2\,NO_3^-\text{ (more concentrated acid)} + 4\,H^+ = Cu^{++} + 2\,NO_2 + 2\,H_2O$$

6. Precipitation of CuS. This is commonly the first step in the separation and identification of copper ions.

$$Cu^{++} + H_2S = \mathbf{CuS}\text{ (black)} + 2\,H^+$$

7. Dissolving of CuS by HNO_3. This is an important step in one method for the separation and detection of copper ions.

$$3\,\mathbf{CuS} + 2\,NO_3^- + 8\,H^+ = 3\,Cu^{++} + 3\,S + 2\,NO + 4\,H_2O$$

8. The precipitation and redissolution of $Cu(OH)_2$ by NH_4OH. This is a means of identifying copper ions and separating them from other cations. The Cu^{++} ion has a coordination number of 4.

$$Cu^{++} + 2\,NH_4OH = \mathbf{Cu(OH)_2}\text{ (blue)} + 2\,NH_4^+$$

$$\mathbf{Cu(OH)_2} + 4\,NH_4OH = Cu(NH_3)_4^{++}\text{ (deep blue)} + 2\,OH^- + 4\,H_2O$$

9. Reduction of Cu(II) to Cu(I) by CN^- ion and formation of the stable complex dicyanocuprate(I) ion. This reaction provides a means for detecting cadmium in the presence of copper. Because the $Cu(CN)_2^-$ ion is very stable it does not yield a high enough concentration of Cu^+ ions to form a precipitate of Cu_2S when the solution is saturated with H_2S. By contrast, the $Cd(CN)_4^{--}$ ion, which forms when Cd^{++} reacts with CN^-, is relatively unstable and yields enough Cd^{++} ions to form a precipitate of CdS with H_2S.

$$2\,Cu(NH_3)_4^{++} + 5\,CN^- + H_2O = 2\,Cu(CN)_2^- + CNO^- + 6\,NH_3 + 2\,NH_4^+$$

10. Reduction of Cu(II) to Cu(I) and, eventually, to Cu(0) by hydrosulfite ion ($S_2O_4^{--}$). This can serve as a useful reaction in the detection of cadmium in the presence of copper, since cadmium ions are not reduced by $S_2O_4^{--}$.

$$2\,Cu(NH_4)_3^{++} + S_2O_4^{--} + 2\,H_2O = 2\,Cu^+ + 2\,SO_3^{--} + 4\,NH_4^+ + 4\,NH_3$$

$$2\,Cu^+ + S_2O_4^{--} + 2\,H_2O = 2\,SO_3^{--} + 2\,\mathbf{Cu} + 4\,H^+$$

11. Commercial preparation of basic $CuCO_3$ by interacting of Na_2CO_3 and $CuSO_4$ solutions:

$$2\,Cu^{++} + CO_3^{--} + 2\,OH^- = \mathbf{CuCO_3 \cdot Cu(OH)_2}$$

12. Commercial preparation of Bordeaux mixture by interaction of $Ca(OH)_2$ and $CuSO_4$ solutions:

$$Ca^{++} + 2\,OH^- + Cu^{++} + SO_4^{--} = \mathbf{Cu(OH)_2} + \mathbf{CaSO_4}$$

Questions

1. For each of the metals silver, mercury, and copper, give: (a) the name and formula of an important ore; (b) a brief description of the metallurgical process by which the pure metal is commercially prepared from this ore; (c) the important uses of the pure metal and the properties or property of the metal upon which each use depends; (d) two important commercial compounds and the uses to which these compounds are put; (e) a method whereby the metal can be converted into a solution of its ion; (f) a reaction in which its ion functions as an oxidizing agent; (g) a reaction which can be used for qualitative identification of its cation.

2. Give the names and components of two common alloys of each of the metals copper and silver.

3. Explain in detail what happens in each of the following processes, and give net equations for all reactions involved.

(a) Dissolving of a mixture of Ag, Ag_2S, and AgCl by a solution of NaCN.

(b) The complete photographic process, that is, taking the picture, preparation of the negative, and preparation of a print.

(c) Deposition of a silver mirror on the surface of a piece of glassware.

(d) Electrolytic refining of blister copper.

(e) Ammonium hydroxide is added dropwise, with constant stirring, to a solution containing Cu^{++} ions until an excess has been added; HCl is added dropwise, with constant stirring to this alkaline solution until it is acidic.

(f) One-molar KCN is added to a deep blue solution containing $Cu(NH_3)_4^{++}$ ions until the blue color disappears.

4. Write the net equation for reactions in which:

(a) Ag(I) is reduced to Ag(O).

(b) Hg(II) is reduced to Hg(I).

(c) Hg(II) is reduced to Hg(O).

(d) Cu(II) is reduced to Cu(I).

(e) Cu(II) is reduced to Cu(O).
(f) Cu(I) is reduced to Cu(O).
(g) Cu(I) is oxidized to Cu(II).
(h) Cu(O) is oxidized to Cu(II).
(i) AgCl is dissolved by NH_4OH.
(j) $Cu(OH)_2$ is dissolved by NH_4OH.
(k) Cu_2S is roasted in air.
(l) HgS is roasted in air.

5. How would the theoretical quantities of copper electrodeposited from solutions of $CuSO_4$ and $NaCu(CN)_2$ by the same number of coulombs of electricity compare? Can you suggest reasons why sulfate rather than cyanide baths are used for electrodeposition in the refining of copper?

CHAPTER 27

Lead and Tin

27.1 The elements of group IVA. The physical properties and oxidation states of the group IVA elements are given in Table 21.1. The increase in metallic character of the elements with increase in atomic number is reflected in the increasing density and metallic luster of the element and the increasing basicity of the oxide. Being on the borderline between metals and nonmetals, tin and lead form amphoteric hydroxides. Both have principal oxidation states of +2 and +4.

Lead

27.2 Mine production, in tons (1950): World, 1,820,000; U.S., 431,000 (Missouri, 134,626; Idaho, 100,025; Utah, 44,253; Colorado, 27,007; Arizona, 26,383); Mexico, 262,000; Australia, 244,000; Canada, 169,000; U.S.S.R., 114,000; Yugoslavia, 88,000; Peru, 63,000; French Morocco, 52,000. U.S. imports, 541,864. U.S. consumption, 1,440,000. 1952 U.S. mine production, 380,000. 1952 U.S. imports, 600,000.

27.3 Occurrence. Lead occurs as galena, PbS, cerussite, $PbCO_3$, and anglesite, $PbSO_4$.

27.4 Metallurgy. It is a relatively complex process including concentration by gravity settling and flotation, followed by roasting and smelting (reduction).

$$2\,PbS + 3\,O_2 = 2\,PbO + 2\,SO_2; \quad PbS + 2\,PbO = 3\,Pb + SO_2;$$
$$PbS + 2\,O_2 = PbSO_4; \quad PbS + PbSO_4 = 2\,Pb + 2\,SO_2;$$
$$2\,PbO + C = 2\,Pb + CO_2$$

27.5 Properties (see Table 21.1). Soft, ductile, malleable, mp 327°C, bp 1620°C, density 11.3.

27.6 Uses. It is used in the manufacture of storage battery plates (32.8%), cable covering (15.5%), paint body and paint pigments (11.2%), tetraethyl lead (9.8%), sheet lead, solder (Pb-Sn alloy), type metal (Pb-Sn-Sb-Cu alloy), fusible alloys, bullets, and shot. The uses of

the pure metal are dependent upon its resistance to corrosion, its softness, and its low melting point. Its alloys have conveniently low melting points.

27.7 Important compounds and their uses

1. $2\,PbCO_3 \cdot Pb(OH)_2$, white lead; paint body and paint pigment. The usual component parts of a paint are:

(a) *The vehicle* is the liquid which serves as the medium in which the other components are suspended. Common vehicles are linseed oil, turpentine, water, amyl acetate and other esters, tung, soybean, and other vegetable oils, acetone and other volatile organic compounds.

(b) *The body* is the solid component which gives the paint its capacity for covering surfaces. The common paint bodies are white lead, zinc white (ZnO), titanium white (TiO_2), zinc sulfide (ZnS), lead oxides (PbO, Pb_3O_4), iron oxide (Fe_2O_3), and powdered aluminum.

(c) *The pigment* gives the paint its characteristic color. The body often serves also as the pigment.

(d) *The drier* is a substance which speeds up the rate at which the paint dries. It may be (1) a volatile liquid such as turpentine or chinawood oil which merely increases the evaporation rate, (2) an oxidizing agent such as MnO_2 which augments the oxidation of the linseed oil by air, or (3) a catalytic agent, such as CoO and MnO_2, which speeds up the rate of air oxidation.

2. PbO_2, storage battery plates.

3. $Pb(C_2H_5)_4$, tetraethyl lead; gasoline antiknock component.

4. PbO, litharge; cement, paint, manufacture of PbO_2 and Pb for use in storage battery plates.

5. Pb_3O_4, red lead; paint pigment.

6. $PbCrO_4$, chrome yellow; paint pigment.

7. $Pb_3(AsO_4)_2$; insecticide.

8. PbN_6, lead azide; detonator.

27.8 Reactions (see 27.4)

1. $Pb = Pb^{++} + 2e$; $E^\circ = 0.126$ volt. Lead is not very reactive.

2. Reactions of lead with HNO_3 and aqua regia. These reactions are used in dissolving lead and its alloys.

$$3\,Pb + 2\,NO_3^- + 8\,H^+ = 3\,Pb^{++} + 2\,NO + 4\,H_2O$$

$$3\,Pb + 2\,NO_3^- + 12\,Cl^- + 8\,H^+ = 3\,PbCl_4^{--} + 2\,NO + 4\,H_2O$$

3. Precipitation of PbS in qualitative analysis.

$$Pb^{++} + H_2S = \mathbf{PbS}\ (\text{black}) + 2\,H^+$$

4. Identification of lead ions in qualitative analysis

$$Pb^{++} + SO_4^{--} = \mathbf{PbSO_4}\text{ (white)}$$
$$Pb^{++} + CrO_4^{--} = \mathbf{PbCrO_4}\text{ (yellow)}$$

5. Dissolving of PbS by HNO_3. This is a separation reaction commonly encountered in qualitative analysis.

$$3\,\mathbf{PbS} + 2\,NO_3^- + 8\,H^+ = 3\,Pb^{++} + 3\,S + 2\,NO + 4\,H_2O$$

6. Dissolving of $PbSO_4$ by $NH_4C_2H_3O_2$ solution. This reaction is commonly employed in the separation and identification of lead; $Pb(C_2H_3O_2)_2$ is unique among salts in that it is a weak electrolyte.

$$\mathbf{PbSO_4} + 2\,C_2H_3O_2^- = Pb(C_2H_3O_2)_2 + SO_4^{--}$$

7. Thermal decomposition of PbO_2. This is a laboratory source of oxygen. It demonstrates the relative instability of the +4 oxidation state of lead.

$$2\,PbO_2 = 2\,PbO + O_2\text{ (moderate heating)}$$
$$3\,PbO_2 = Pb_3O_4 + O_2\text{ (intense heating)}$$

8. Oxidation of hydrogen halides by PbO_2. This is a laboratory source of Cl_2 and Br_2. It demonstrates the oxidizing property of the +4 oxidation state of lead.

$$\mathbf{PbO_2} + 2\,Cl^- + 4\,H^+ = Pb^{++} + 2\,H_2O + Cl_2$$

9. Amphoterism of $Pb(OH)_2$. An amphoteric hydroxide is one that will react with both strong acids and strong bases (see 14.7).

$$\mathbf{Pb(OH)_2} + 2\,H^+ = Pb^{++} + 2\,H_2O$$
$$\mathbf{Pb(OH)_2} + 2\,OH^- = Pb(OH)_4^{--}$$

10. *Storage battery reactions* (see 25.14)

(a) Discharge reactions

At lead plate:

$$Pb + SO_4^{--} = PbSO_4 + 2e$$

At PbO_2 plate:

$$PbO_2 + SO_4^{--} + 4\,H^+ + 2e = PbSO_4 + 2\,H_2O$$

(b) Charging reactions

At lead plate:

$$PbSO_4 + 2e = Pb + SO_4^{--}$$

At PbO_2 plate:

$$PbSO_4 + 2\,H_2O = PbO_2 + SO_4^{--} + 4\,H^+ + 2e$$

11. Manufacture of $Pb(C_2H_5)_4$ for use in "ethyl" gasoline

$$4\,C_2H_5Br + 4\,Na\text{-}Pb\ (a\ Pb\text{-}Na\ alloy) = Pb(C_2H_5)_4 + 3\,Pb + 4\,NaBr$$

12. Oxidation of $Pb(C_2H_5)_4$. This occurs in the combustion of ethyl gasoline. Under the conditions that prevail in the cylinder of an automobile, the major over-all reaction is

$$Pb(C_2H_5)_4 + 13\,O_2 = \mathbf{Pb} + 8\,CO_2 + 10\,H_2O$$

As noted in Section 22.11–2, the ethylene bromide which, with $Pb(C_2H_5)_4$, is a component of ethyl gas, converts the Pb formed in the reaction to volatile $PbBr_2$. Deposition of lead in the cylinder is thereby prevented.

13. Commercial preparation of PbO_2 and spongy lead by electrolytic oxidation and reduction of PbO. In the manufacture of storage battery plates the grids are first impregnated with PbO and one is attached to the positive pole and the other to the negative pole of an electrolytic cell in which the electrolyte is NaOH. At the positive pole PbO is oxidized to PbO_2.

$$PbO + 2\,OH^- = PbO_2 + H_2O + 2e$$

At the negative pole PbO is reduced to Pb.

$$PbO + 2\,H^+ + 2e = Pb + H_2O$$

The Pb and PbO_2 that are formed have the sponginess necessary to give the large surface desired in storage battery plates.

Tin

27.9 Mine production in tons (1950): World, 166,400; Malaya, 57,537; Indonesia, 32,099; Bolivia, 31,213; Belgian Congo, 13,700; Thailand, 10,364; Nigeria, 8258; U.S. 15. U.S. consumption, 129,883. U.S. imports, 108,797. It is obvious from these figures that the U.S. is completely dependent upon outside sources for the large tonnages of tin which it consumes.

27.10 Occurrence. Cassiterite, SnO_2, is the only important ore.

27.11 Metallurgy. Concentration by gravity settling and flotation followed by reduction with coke are the major processes involved.

$$SnO_2 + C = Sn + CO_2$$

27.12 Properties (see Table 27.1). Mp 232°C; bp 2260°C; density 7.3; ductile; malleable; attractive color; relatively inactive; does not tarnish.

27.13 Uses. It is used in the manufacture of tin plate (41%), solder (21%), bronze and brass (20%), babbitt (6.2%), tinning metal (2.8%), type metal (2.4%).

Tinplate, used in the manufacture of tin cans and other products, is sheet iron coated with a film of tin. This film is applied by passing the sheet iron, in the form of a continuous ribbon, through either a bath of molten tin or an electrolytic bath containing a tin salt in which the iron ribbon is the negative pole (see Figure 27.1). The following qualities make tin a very desirable plating material: (a) attractive color; (b) very slight tendency to tarnish; (c) low reactivity; (d) strong tendency to

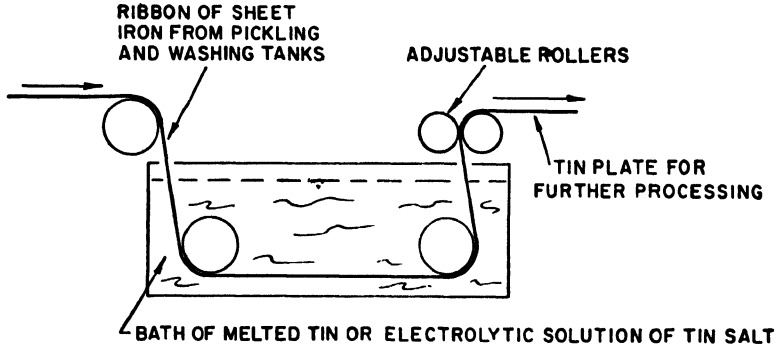


Figure 27.1. The manufacture of tin plate.

adhere to iron; (e) failure of the film to break when the plate is crimped, as in the making of tin cans. One of the undesirable features of tin plate is the fact that, because of the softness of the tin, the film is easily scratched through. This exposes the underlying iron sheet and allows it to rust. The corrosion of the iron is speeded up as a consequence of the action of the iron-tin battery that is formed when the scratch is made. The details of this reaction will be discussed in Section 29.6.

Babbitt metal is an alloy of tin, antimony, and copper; it is used for bearing linings in engines and heavy machinery.

27.14 Important commercial compounds and their uses. Stannous and stannic chlorides ($SnCl_2$ and $SnCl_4$) will yield mordants in dyeing. A fabric which will not take a particular dye can be dyed by impregnating it with a solid substance called a *mordant*, which will ad-

sorb the dye in question. In the mordant-dyeing process the fabric is first soaked in a solution of $SnCl_2$ or $SnCl_4$ and is then given an alkaline wash. This causes $Sn(OH)_2$ and $Sn(OH)_4$ to be precipitated in a very finely divided condition in the threads of the fabric; these solids then act as mordants, that is, they adsorb the dye or dyes with which the fabric is to be tinted. At the same time they add weight and body to the fabric. *Adsorption* is the adherence of one substance to the *surface* of another substance. The reason why mordants such as $Sn(OH)_2$ and $Sn(OH)_4$ have unique ability to adsorb certain dyes is not well understood.

27.15 Reactions

1. $Sn = Sn^{++} + 2e$; $E^\circ = 0.136$ volt

2. Reaction of tin with nitric acid. This reaction can be used as a means of separating tin from other metals in an alloy.

$$2\,Sn + 4\,NO_3^- + 4\,H^+ = 3\,\mathbf{SnO_2} + 4\,NO + 2\,H_2O$$

In the presence of an oxidizing agent (HNO_3), a polyvalent metal (Sn) will take a higher oxidation state. As a general rule as the oxidation state of a metal increases, its oxide becomes more acidic, less basic. Whereas a basic oxide will dissolve in nitric acid to form a soluble salt (nitrate), an acidic oxide will not react further with this acid. Tin has its higher oxidation number, +4, in SnO_2; for that reason SnO_2 is acidic in character and does not dissolve in HNO_3 to form a nitrate (see 18.13–2).

3. Precipitation of SnS and SnS_2. This reaction can serve as the first step in the separation and identification of tin.

$$Sn^{++} + H_2S = \mathbf{SnS}\ \text{(dark brown)} + 2\,H^+$$
$$Sn^{+4} + 2\,H_2S = \mathbf{SnS_2}\ \text{(yellow)} + 4\,H^+$$

4. Dissolving SnS_2 by ammonium sulfide. This reaction can serve as the basis for the separation of tin sulfide from other metal sulfides.

$$\mathbf{SnS_2} + S^{--} = SnS_3^{--}$$

5. The amphoteric character of $Sn(OH)_2$ (see 14.7)

$$\mathbf{Sn(OH)_2} + 2\,H^+ = Sn^{++} + 2\,H_2O$$
$$\mathbf{Sn(OH)_2} + 2\,OH^- = Sn(OH)_4^{--}\ \text{(tetrahydroxostannate(II) ion)}$$

6. Oxidation of Sn(II) to Sn(IV) by various oxidizing agents. These reactions illustrate the strong reducing action of tin(II) compounds.

$Hg^{++} + Sn^{++} = Sn^{+4} + Hg$

$2\,\mathbf{Bi(OH)_3} + 3\,Sn(OH)_4^{--} = 2\,\mathbf{Bi} + 3\,Sn(OH)_6^{--}$

$Cr_2O_7^{--} + 3\,Sn^{++} + 14\,H^+ = 2\,Cr^{+3} + 3\,Sn^{+4} + 7\,H_2O$

$2\,MnO_4^- + 3\,Sn(OH)_4^{--} + 4\,H_2O = 2\,\mathbf{MnO_2} + 3\,Sn(OH)_6^{--} + 2\,OH^-$

$2\,Fe^{+++} + Sn^{++} = 2\,Fe^{++} + Sn^{++++}$

Questions

1. For each of the elements, tin and lead, give: (a) the name and formula of the most important ore; (b) a brief description of the process by which the metal is obtained from this ore; (c) two important industrial uses and the properties upon which these uses depend; (d) the names and components of two important alloys; (e) two important commercial compounds and the use of each; (f) a reaction whereby the metal is converted into a solution of its ions; (g) a reaction that can be used for the qualitative identification of its ion; (h) a reaction in which its compound or ion functions as an oxidizing agent; (i) a reaction in which its compound or ion functions as a reducing agent.

2. Explain, with the aid of all necessary equations, the statement, "the hydroxides of lead and tin are amphoteric."

3. Describe, with the aid of equations, what happens: (a) when a lead storage battery delivers current; (b) when a discharged lead storage battery is recharged.

4. Account for the fact that tinplate rusts rapidly when the covering sheet of tin is fractured and the iron is exposed.

5. List the usual components of a paint and point out the function of each.

CHAPTER 28

Arsenic, Antimony, Bismuth

28.1 The elements of group VA. The physical properties, electronic configurations, and oxidation states of the group VA elements are given in Table 18.1, page 358. The information given in this table, coupled with the chemical behavior of the five elements and their compounds, emphasizes the fact that as the atomic number increases, the elements become less nonmetallic and more metallic, and their oxides become less acidic and more basic. Nitrogen and phosphorus are nonmetals, the former being the more electronegative. Arsenic, we shall find, is likewise distinctly nonmetallic in character, its oxides being distinctly acidic, although its ternary acids H_3AsO_3 and H_3AsO_4 are weaker than the analogous H_3PO_3 and H_3PO_4. That antimony has the character of a metal is indicated by the fact that Sb^{+++} ions exist in solution; however, Sb_2O_5 is distinctly acidic. The oxide Sb_2O_3 is amphoteric in character. Likewise the compound SbH_3 (stibine) is less stable than AsH_3 (arsine), which is in turn less stable than the binary hydrogen compounds of nitrogen and phosphorus. Bismuth is definitely a metal; Bi^{+++} ions exist in solution, Bi_2O_3 is distinctly basic in character, and BiH_3 is so unstable that it cannot be isolated. Bismuth has an oxidation state of +5 only in the unstable bismuthates such as $NaBiO_3$. The increase in density, hardness, luster, and conductivity of the elements with increase in atomic number is indicative of the increase in metallic character.

Although arsenic is definitely nonmetallic, it is discussed with antimony and bismuth rather than with nitrogen and phosphorus because its qualitative separation and identification throw it more logically in a class with the former.

Arsenic

28.2 Mine production of As_2O_3 in tons (1950): World, 47,200; U.S., 13,200; Mexico, 9900; Belgium, 2100; Japan, 1790. U.S. imports, 14,774. U.S. consumption, 32,104.

28.3 Occurrence. Arsenic occurs as arsenopyrite, FeAsS; orpiment, As_2S_3; and realgar, As_2S_2.

28.4 Metallurgy. It is recovered as As_2O_3 (white arsenic) from flue dust in the metallurgy of Cu, Zn, and Pb (Figure 28.1). Arsenic is obtained by reduction of this As_2O_3 with coke.

$$2\,FeAsS + 5\,O_2 = Fe_2O_3 + As_2O_3 + 2\,SO_2$$
$$2\,As_2O_3 + 3\,C = 4\,As + 3\,CO_2$$

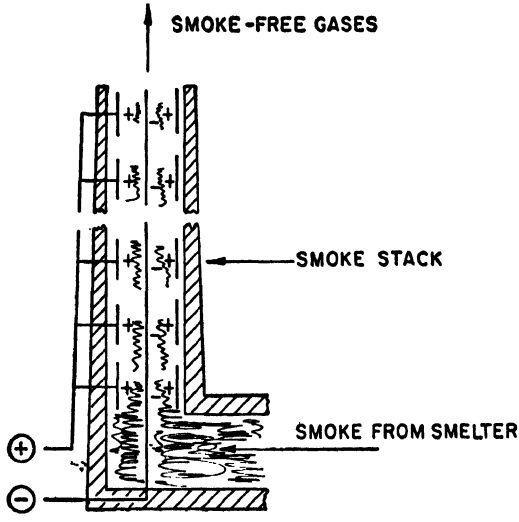


Figure 28.1. Cottrell precipitator for the recovery of As_2O_3 from smelter flue gases. The As_2O_3, formed when the arsenic-bearing Cu, Zn and Pb ores are roasted, sublimes in the smelter and solidifies as fine, negatively-charged dust particles (smoke) in the stack. These negatively-charged particles are attracted to and collect on the positive electrodes from which they are subsequently removed. The gases that escape from the stack are smoke-free. Ordinary smoke, due to finely divided carbon (coal) particles, may be eliminated by Cottrell precipitators.

28.5 Properties (see Table 18.1). Its significant properties are: nonmetallic in character; brittle, gray solid; sublimes when heated; density 5.7.

28.6 Uses. The major use of arsenic is in the form of its compounds whose toxicity makes them valuable as insecticides, weed killers, and wood preservatives; As_2O_3 is the source of these compounds. A small amount of elemental arsenic is used in the lead-arsenic alloy out of which battery grids and lead shot are made; the lead-arsenic alloy is much harder than pure lead; as a result the grids made from this alloy are

rigid enough to hold their shape and the shot is hard enough to resist deformation.

28.7 Important commercial compounds and their uses

1. $Pb_3(AsO_4)_2$ and $Ca_3(AsO_4)_2$, insecticides
2. Na_3AsO_4, insecticide and weed killer
3. As_2O_3, insecticide, weed killer, preservative in taxidermy, manufacture of glass. In the latter use the As_2O_3, being acidic, reacts with the basic components of glass, Na_2O, CaO, K_2O, PbO, etc.
4. Na_3AsO_3, weed killer, wood preservative, and insecticide

28.8 Reactions

1. Reaction with nitric acid. The formation of arsenic acid rather than a solution of arsenic nitrate shows the nonmetallic character of arsenic.

$$3\,As + 5\,NO_3^- + 5\,H^+ + 2\,H_2O = 3\,H_3AsO_4 + 5\,NO$$

2. Precipitation of As_2S_3 and As_2S_5. These are important reactions in the analytical separation and identification of arsenic.

$$2\,H_3AsO_4 + 5\,H_2S = As_2S_5\ (\text{yellow}) + 8\,H_2O$$
$$2\,H_3AsO_3 + 3\,H_2S = As_2S_3\ (\text{yellow}) + 6\,H_2O$$

3. Reaction of As_2S_3 and As_2S_5 with a solution of $(NH_4)_2S$. This reaction can serve as the basis for the separation of arsenic from lead, mercury, copper, bismuth, and cadmium, since the sulfides of the latter five metals do not react with $(NH_4)_2S$.

$$As_2S_3 + 3\,S^{--} = 2\,AsS_3^{---}$$
$$As_2S_5 + 3\,S^{--} = 2\,AsS_4^{---}$$

The molecular equations for these reactions are

$$As_2S_3 + 3\,(NH_4)_2S = 2\,(NH_4)_3AsS_3$$
$$As_2S_5 + 3\,(NH_4)_2S = 2\,(NH_4)_3AsS_4$$

The compounds $(NH_4)_3AsS_3$ and $(NH_4)_3AsS_4$ are ammonium salts of the thio-acids H_3AsS_3 and H_3AsS_4, just as Na_3AsO_3 and Na_3AsO_4 are salts of the oxy-acids H_3AsO_3 and H_3AsO_4. The two thio-salts are typical strong electrolytes and ionize to give NH_4^+ ions and the complex ions AsS_3^{---} and AsS_4^{---}.

4. Decomposition of the thio-acids of arsenic. The acids H_3AsS_3 and H_3AsS_4 are very unstable, decomposing to form H_2S and As_2S_3 and As_2S_5. For that reason, As_2S_3 and As_2S_5 are precipitated when a solution

containing AsS_3^{---} or AsS_4^{---} ions is made acidic. This reaction is significant in the qualitative separation and identification of arsenic.

$$2\,AsS_3^{---} + 6\,H^+ = \mathbf{As_2S_3} + 3\,H_2S$$
$$2\,AsS_4^{---} + 6\,H^+ = \mathbf{As_2S_5} + 3\,H_2S$$

5. Arsenites act as reducing agents (see Table 20.1)

$$2\,MnO_4^- + 5\,H_3AsO_3 + 6\,H^+ = 2\,Mn^{++} + 5\,H_3AsO_4 + 3\,H_2O$$

6. Identification of H_3AsO_4 and the arsenate ion

$AsO_4^{---} + 3\,Ag^+ = \mathbf{Ag_3AsO_4}$ (chocolate brown) (see 26.13–6)

$AsO_4^{---} + Mg^{++} + NH_4^+ = \mathbf{MgNH_4AsO_4}$ (white)

7. *The Marsh test for arsenic.* This test, widely used in toxicology for detection of arsenic poisoning, depends on the fact that the unstable compound arsine (AsH_3) is formed when an arsenic compound is reduced by an active metal, zinc, in acid solution. This arsine yields a black, shiny deposit of arsenic when it is either incompletely oxidized or thermally decomposed. This black deposit can be dissolved by a solution of sodium hypochlorite, NaClO. The material to be tested is placed in a generator in which hydrogen gas is being liberated by the reaction of pure arsenic-free zinc on pure arsenic-free sulfuric acid. Any arsenic compound present in the sample will be reduced to AsH_3. When the escaping hydrogen is ignited, the AsH_3 will burn with a characteristic violet-blue flame. The As_2O_3 which is formed in the combustion process is a white solid and will cause a white smoke to be formed. If the violet-blue flame is chilled by insertion of a piece of white porcelain, a black, shiny deposit of arsenic will form. If the glass tube through which the H_2 and AsH_3 gases are escaping from the generator is heated, the AsH_3 will decompose and a black deposit of arsenic will form on the inside of the tube. The arsenic deposit is soluble in NaClO solution. The evidence of all the tests listed above, namely, (1) the violet-blue flame, (2) the white smoke, and (3) the black deposit which is soluble in NaClO, shows the presence of arsenic in the sample. It should be noted that antimony, which forms stibine (SbH_3), will give a similar colored flame and similar black deposits, but the latter are not soluble in NaClO.

The following reactions take place in the Marsh test:

$$6\,Zn + As_2O_3 + 12\,H^+ = 2\,AsH_3 + 3\,H_2O + 6\,Zn^{++}$$
$$2\,AsH_3 + 3\,O_2 = 3\,H_2O + \mathbf{As_2O_3}\ \text{(white smoke, violet-blue flame)}$$
$$4\,AsH_3 + 3\,O_2 = 6\,H_2O + 4\,\mathbf{As}\ \text{(black deposit)}$$
$$2\,AsH_3\ \text{(heated)} = 3\,H_2 + 2\,\mathbf{As}\ \text{(black deposit)}$$
$$2\,\mathbf{As} + 5\,ClO^- + 3\,H_2O = 2\,H_3AsO_4 + 5\,Cl^-$$

8. Manufacture of Na_3AsO_3 and arsenates from As_2O_3

$$As_2O_3 + 6\,Na^+ + 6\,OH^- = 2\,Na_3AsO_3 + 3\,H_2O$$
$$As_2O_3 + 2\,ClO^- + 6\,OH^- = 2\,AsO_4^{---} + 2\,Cl^- + 3\,H_2O$$

Antimony

28.9 Mine production in tons (1950): World, 55,000; Union of South Africa, 9100; Mexico, 6450; U.S. 2490; Czechoslovakia, 2200. U.S. imports, 9746. U.S. consumption, 15,494.

28.10 Occurrence. The only important ore is stibnite, Sb_2S_3.

28.11 Metallurgy. Antimony is prepared by reduction of stibnite (Sb_2S_3) with scrap iron or roasting of Sb_2S_3 and reduction of the Sb_2O_3 with carbon.

$$Sb_2S_3 + 3\,Fe = 2\,Sb + 3\,FeS$$
$$2\,Sb_2S_3 + 9\,O_2 = 2\,Sb_2O_3 + 6\,SO_2$$
$$2\,Sb_2O_3 + 3\,C = 4\,Sb + 3\,CO_2$$

28.12 Properties (see Table 18.1). Some significant properties of antimony are: silvery-gray color, metallic luster, hard, brittle, mp 630.5°C, bp 1380°C, density 6.68, expands when it freezes. The latter property makes it particularly valuable for making printing type because it insures a clean-cut reproduction of the casting mold.

28.13 Uses. Its important uses are: antimony-lead alloy containing 1–2% Sb for use in making storage battery grids (45%); pewter (Pb-Sn-Sb-Cu), type metal, babbitt, and other bearing alloys (25%); Sb_2O_3 (20%); Sb_2S_3 (8%).

28.14 Important compounds and their uses

1. Sb_2O_3. It is used in the manufacture of ceramic enamels, paints, lacquers, and textiles.
2. Sb_2S_3. It is used in making matches and red rubber (see 19.6–4).

28.15 Reactions (see 28.11)

1. Reaction of Sb with HNO_3. The formation of Sb_2O_5 rather than a solution of cations shows the acidic character of the antimony(V) oxide. This identifies antimony as being nonmetallic in character (see 18.13–2).

$$6\,Sb + 10\,NO_3^- + 10\,H^+ = 3\,Sb_2O_5\ (\text{white}) + 10\,NO + 5\,H_2O$$

There is evidence that Sb_2O_4 is formed in this reaction.

2. Reaction of Sb with aqua regia

$$3\,Sb + 5\,NO_3^- + 20\,H^+ + 18\,Cl^- = 3\,SbCl_6^- + 5\,NO + 10\,H_2O$$

3. Hydrolysis of antimony(III) halides to give insoluble basic salts containing the antimonyl radical SbO^+. In the presence of excess H^+ ions the reaction is reversed and hydrolysis is prevented.

$$Sb^{+++} + Cl^- + H_2O \rightleftarrows \mathbf{SbOCl}\ \text{(white)} + 2\,H^+$$

4. Precipitation of antimony sulfide in the analytical separation and identification of ions. This can serve as a confirmatory test for antimony.

$$2\,Sb^{+++} + 3\,H_2S = \mathbf{Sb_2S_3}\ \text{(orange)} + 6\,H^+$$

$2\,SbCl_4^-$ (in high concentrations of Cl^- ions)

$$+ 3\,H_2S = \mathbf{Sb_2S_3} + 6\,H^+ + 8\,Cl^-$$

5. Formation of soluble salts of thioantimonic acid and reprecipitation of Sb_2S_3. Note the similarity between antimony, arsenic, and tin (see 28.8–3, 28.8–4, and 27.15–4).

$$\mathbf{Sb_2S_3} + 3\,(NH_4)_2S = 2\,(NH_4)_3SbS_3$$

$$\mathbf{Sb_2S_3} + 3\,S^{--} = 2\,SbS_3^{---}\ \text{(complex trithioantimonate(III) ion)}$$

$$2\,SbS_3^{---} + 6\,H^+ = \mathbf{Sb_2S_3} + 3\,H_2S$$

6. Amphoterism of $Sb(OH)_3$. This is in line with its position in the periodic table on the borderline between metals and nonmetals (see 14.7).

$$\mathbf{Sb(OH)_3} + 3\,H^+ = Sb^{+++} + 3\,H_2O$$

$$\mathbf{Sb(OH)_3} + OH^- = Sb(OH)_4^-$$

Bismuth

28.16 Smelter production in tons (1950) (smelter production includes metal produced from both domestic and imported ores): World, 1650; Mexico, 289; Canada, 110. U.S. imports, 390.

28.17 Occurrence. Glance, Bi_2S_3; small amount of native bismuth.

28.18 Metallurgy. It is a by-product in the refining of lead and copper. The ore is roasted and reduced with coke. The separation of bismuth from other metals is an involved procedure; this, plus its scarcity, makes the metal very expensive.

$$Bi_2S_3 + 6\,O_2 = 2\,Bi_2O_3 + 3\,SO_2$$

$$2\,Bi_2O_3 + 3\,C = 4\,Bi + 3\,CO_2$$

28.19 Properties (see Table 18.1). Bismuth has the following properties: hard, brittle, metallic luster, silvery-red color, mp 271°C, bp 1470°C, density 9.8, expands slightly on freezing.

28.20 Uses. About 65% of the bismuth consumed in the U.S. is used for making fusible (low-melting) alloys and type metal alloys; about 25% is used for making pharmaceuticals, mostly for treatment of stomach disorders. The compositions and melting points of some typical low-melting (fusible) alloys are given in Table 28.1. These alloys are

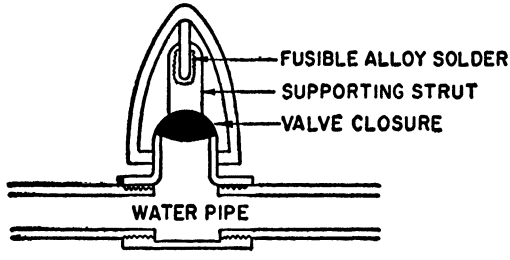


Figure 28.2. Sprinkler head of automatic sprinkler system. The heat of a fire melts the fusible-alloy solder which binds together the two parts of the supporting strut. This causes the strut to collapse, thereby releasing the valve closure and allowing the water to escape from the pipe into the fire area.

used in making safety plugs or links for automatic fire extinguisher systems, fire curtains, fire doors, and boiler control switches (see Figure 28.2). The low melting point of these alloys illustrates the principle that a solute lowers the freezing point (melting point) of a solvent.

Each metal can be looked upon as either a solute or a solvent.

TABLE 28.1

LOW MELTING ALLOYS

Alloy	Mp °C (softening point) of alloy	Melting point of pure component metal; per cent in alloy			
		Pb 327.5°C	Sn 232°C	Bi 271°C	Cd 321°C
Newton's metal	94.5	31	19	50	
Rose's metal	93.8	28	22	50	
Wood's metal	70.5	25	12.5	50	12.5

28.21 Important compounds and their uses. Both $BiONO_3 \cdot H_2O$, bismuthyl nitrate and $BiOHCO_3$, bismuthyl carbonate are used as internal medicines.

28.22 Reactions of bismuth and its compounds

1. Reaction of Bi with HNO_3. The fact that Bi^{+++} ions are formed shows that bismuth is metallic in character. This emphasizes the increase in metallic character of the group VA elements with increase in atomic number.

$$Bi + NO_3^- + 4\,H^+ = Bi^{+++} + NO + 2\,H_2O$$

2. Hydrolysis of bismuth halides to form the insoluble basic salt containing the bismuthyl radical, BiO^+. This shows the similarity between bismuth and antimony. As with antimony salts, the hydrolysis is prevented by the presence of sufficient hydrogen ions (see 28.15–B).

$$Bi^{+++} + Cl^- + H_2O \rightleftarrows \mathbf{BiOCl}\ (\text{white}) + 2\,H^+$$

3. Precipitation of bismuth sulfide in the analytical separation

$$2\,Bi^{+++} + 3\,H_2S = \mathbf{Bi_2S_3}\ (\text{black}) + 6\,H^+$$

4. Dissolving of Bi_2S_3 by nitric acid. This can serve as an essential step in the analytical separation and identification of bismuth.

$$\mathbf{Bi_2S_3} + 2\,NO_3^- + 8\,H^+ = 2\,Bi^{+++} + 2\,NO + 3\,S + 4\,H_2O$$

5. The reduction of bismuth hydroxide by stannate(II) ions. This reaction illustrates the reducing power of tin(II) compounds and the low electropositivity of bismuth, and the consequent oxidizing power of bismuth hydroxide.

$$2\,\mathbf{Bi(OH)_3} + 3\,Sn(OH)_4^{--} = 2\,\mathbf{Bi}\ (\text{black}) + 3\,Sn(OH)_6^{--}$$

6. The oxidizing power of bismuth(V) compounds. In group VA as the atomic number of the element increases, the stability of its higher oxidation states decreases. Since the higher oxidation state compounds of an element generally are oxidizing agents, it follows that if these compounds are unstable they will have powerful oxidizing action. The presence of bismuth in the BiO_3^- radical illustrates the fact that as the oxidation number of an element increases its compounds become more acidic in character. The compound $HBiO_3$ is a very weak acid.

$$2\,Mn^{++} + 5\,HBiO_3 + 9\,H^+ = 5\,Bi^{+++} + 2\,MnO_4^- + 7\,H_2O$$

This reaction can serve as a confirmatory test for Mn^{++} ions. The bismuthate is added as a reagent in the form of solid $NaBiO_3$.

Questions

1. What change in character of the elements of group VA takes place as the atomic number increases? How is this change related to the change in atomic diameter?

2. For each of the elements arsenic, antimony, and bismuth: (a) give the name and formula of an ore; (b) indicate briefly how it is prepared from its ore; (c) list the important uses of the element; (d) list the important compounds and their uses; (e) indicate how the ion formed by the element may be identified.

3. Which of the following is the strongest oxidizing agent: H_3AsO_4, Sb_2O_5, $HBiO_3$?

4. Which compound is the most stable toward heat, which the least stable: NH_3, PH_3, AsH_3, SbH_3, BiH_3?

5. When As, Sb, and Bi, respectively, are treated with concentrated nitric acid, soluble H_3AsO_4, insoluble Sb_2O_5, and soluble Bi^{+++} are formed. Account for the differences in behavior.

6. Give the detailed electronic configurations (*s*, *p*, *d*, and *f* orbitals) of the arsenic, antimony, and bismuth atoms.

CHAPTER 29

Zinc and Cadmium

29.1 The elements of group IIB. The physical properties, atomic configurations, and oxidation states of the group IIB elements are given in Table 29.1. As already noted in Chapter 26, mercury is discussed along with gold, silver, and copper because of its closer similarity to the IB group elements than to zinc and cadmium.

TABLE 29.1

PROPERTIES OF ZINC, CADMIUM, AND MERCURY

Element	Period	At. no.	At. wt	At. diam	Configuration	Density	Mp	Bp	Color and state	Oxid. state
Zinc	4	30	65.38	2.76 Å	2, 8, 18, 2	7.14 g/cc	420°C	907°C	silver-white, solid	2
Cadmium	5	48	112.4	3.08 Å	2, 8, 18, 18, 2	8.64 g/cc	321°C	765°C	silver-white, solid	2
Mercury	6	80	200.6	3.14 Å	2, 8, 18, 32, 18, 2	13.55 g/cc	−38.9°C	357°C	silver-white, liquid	1, 2

Zinc and cadmium look alike and are similar with respect to both physical properties and chemical behavior. They both have one stable oxidation state, +2. Although zinc is more electropositive, having an oxidation potential of 0.763 volt as compared with a potential of 0.403 for cadmium, its hydroxide is amphoteric, whereas $Cd(OH)_2$ is characteristically basic, showing no acidic behavior. The electropositivity of the elements in group IIB increases as the atomic number decreases. This is in direct contrast to the group IIA behavior, where the electropositivity and the oxidation potential increase as the atomic number increases.

Zinc is the more abundant of the two elements in nature. Cadmium always occurs in zinc ores, and the metal is essentially a by-product of the zinc industry.

Zinc

29.2 Mine production in tons (1950): World, 2,320,000; U.S., 622,000; Canada, 311,000; Mexico, 245,000; Australia, 216,000; U.S.S.R., 141,500; Italy, 93,000; Belgian Congo, 84,000; Peru, 81,000; German Federal Republic, 76,000. U.S. imports, 428,512. U.S. consumption, 1,149,000. From the standpoint of tonnage of metal consumed zinc falls in a class with copper, lead, and aluminum.

29.3 Occurrence. Sphalerite, ZnS; smithsonite, $ZnCO_3$; and zincite, ZnO are the important ores.

29.4 Metallurgy. The process involves concentration by flotation followed by (a) roasting and reduction with coke, or (b) leaching with sulfuric acid and electrodeposition.

The latter process appears to be gaining in favor because, in addition to giving high purity zinc, it allows for easy removal of cadmium, silver, and copper; zinc metal, added to the leach liquor before electrolysis, causes these three metals to be precipitated out.

The reactions that take place during the metallurgical process are shown below.

$$2\,ZnS + 3\,O_2 = 2\,ZnO + 2\,SO_2$$
$$ZnO + C = Zn + CO$$

Because the reduction temperature is high, due to the stability of ZnO, the product is CO rather than CO_2. The zinc, having a boiling point of only 907°C, distills off and is condensed.

$$ZnS\ (ZnCO_3, ZnO) + 2\,H^+ = Zn^{++} + H_2S\ (H_2O, CO_2)$$
$$Zn + Cu^{++}\ (2\,Ag^+, Cd^{++}) = Zn^{++} + Cu\ (2\,Ag, Cd)$$
$$Zn^{++} + 2e = Zn$$

29.5 Properties (see Table 29.1). Zinc is a moderately hard, brittle metal which contracts only slightly when it freezes. It is not very malleable or ductile.

29.6 Uses. It is used for the manufacture of galvanized iron (50%), sheet zinc (20%), zinc-base alloys of which the most important is brass (Zn-Cu) (7.7%), ZnO and ZnS (1.4%), and $ZnCl_2$. Galvanized iron is sheet iron covered with a film of zinc. The film is applied by allowing the ribbon of sheet iron to pass through a tank of molten zinc or an electrolysis bath. Zinc adheres to iron about as well as does tin.

The main object in coating iron with zinc and tin is to protect it

from air and moisture so that it will not rust. If the film of tin on a piece of tin plate is punctured, the exposed iron will immediately begin to rust as soon as it comes in contact with moisture and air. In contrast, if the film of zinc on a piece of galvanized iron is punctured, the exposed iron does not rust. The explanation is as follows: As noted in Section 25.14A, when two metals are brought in contact with each other in the presence of an electrolyte, a reaction referred to as galvanic action begins to take place, and a battery is created. The more electropositive metal goes into solution (corrodes) and becomes the negative pole of the battery. No corrosion takes place on the surface of the less active metal, which becomes the positive pole. In galvanized iron, the zinc is the more active metal. Therefore, when the zinc film is punctured and water containing dissolved electrolyte such as carbonic acid comes in contact with the punctured region, a galvanic cell is set up in which the zinc corrodes, while the iron does not corrode. As a matter of fact the corrosion of the zinc actually keeps the iron from corroding. This protection does not, however, extend over a large area of iron.

When a piece of tinplate is punctured and water containing electrolyte comes in contact with the exposed area, the iron, being more electropositive than tin, becomes the negative pole in a battery. Because of the galvanic action of this battery the rate of corrosion of the exposed iron is more rapid than if no tin were in contact with it.

The question may arise as to why galvanized iron is not always used in place of tin plate. The answer is that the high reactivity which causes zinc to protect iron makes it unsatisfactory for the many uses to which tinplate, with its coating of relatively inactive tin, is put.

Most of the sheet zinc is used in the manufacture of dry batteries (see 25.14B).

29.7 Important commercial compounds and their uses

1. ZnO, zinc white. Paint body and pigment (see 27.7–1); filler in automobile tires; manufacture of glazes, enamels, and glass.

2. ZnS. Paint body and pigment.

3. $ZnCl_2$. Wood preservative; manufacture of parchment paper. The $ZnCl_2$ has fungicidal action. Accordingly, decay of wood is prevented by soaking it in a solution of this compound. The use of $ZnCl_2$ in the manufacture of parchment paper depends upon its ability to convert wood cellulose into a gelatinized product.

29.8 Reactions (see 29.4)

1. $Zn = Zn^{++} + 2e$; $E^\circ = 0.763$ volt

2. Liberation of H_2 by zinc from dilute nonoxidizing acids. This is the usual laboratory source of hydrogen.

$$Zn + 2\,H^+ = Zn^{++} + H_2$$

3. Liberation of hydrogen by zinc from steam at high temperatures

$$Zn + H_2O = ZnO + H_2$$

4. Liberation of hydrogen by zinc from solutions of strong alkalis

$$Zn + 2\,OH^- + 2\,H_2O = Zn(OH)_4^{--} \text{ (tetrahydroxozincate ion)} + H_2$$

5. Dissolving of zinc in concentrated HNO_3

$$3\,Zn + 2\,NO_3^- + 8\,H^+ = 3\,Zn^{++} + 2\,NO + 4\,H_2O$$

6. Replacement of metal ions by zinc in the metallurgy of silver and zinc

$$Zn + 2\,Ag^+\ (Cd^{++}, Cu^{++}) = Zn^{++} + 2\,Ag\ (Cd, Cu)$$

7. Amphoterism of $Zn(OH)_2$ (see 14.7). This is in keeping with the position of zinc along the borderline between the metals and nonmetals. This reaction is important in the analytical separation of zinc.

$$\mathbf{Zn(OH)_2} + 2\,H^+ = Zn^{++} + H_2O$$
$$\mathbf{Zn(OH)_2} + 2\,OH^- = Zn(OH)_4^{--}$$

8. Formation of the complex tetraminezinc ion in the analytical separation of zinc

$$\mathbf{Zn(OH)_2} + 4\,NH_3 = Zn(NH_3)_4^{++} + 2\,OH^-$$

9. Precipitation of zinc sulfide. This reaction occurs in the analytical separation and identification of zinc.

$$Zn^{++} + H_2S = \mathbf{ZnS}\ \text{(white)} + 2\,H^+$$

10. Commercial preparation of $ZnCl_2$

$$ZnO + 2\,H^+ + 2\,Cl^- = ZnCl_2 + H_2O$$

11. Identification of zinc

$$3\,Zn^{++} + 2\,Fe(CN)_6^{----} + 2\,K^+ = \mathbf{Zn_3K_2[Fe(CN)_6]_2}\ \text{(grayish white)}$$

12. Reactions in the dry battery and the Daniell cell (see 25.14B)

Cadmium

29.9 Mine production in tons (1950): World, 6170; U.S., 4580; Southwest Africa, 865; Mexico, 758; Canada, 416; Australia, 316. U.S. imports, 1115. U.S. consumption, 4812.

29.10 Occurrence. Cadmium occurs largely as greenockite, CdS, and is generally found in zinc ore deposits.

29.11 Metallurgy. It is recovered as a by-product in the metallurgy of zinc. Cadmium is separated from zinc by replacement by zinc, as noted in Section 29.4, or by fractional distillation of the mixture of zinc and cadmium obtained in the roasting-reduction process (bp of zinc is 907°C, of cadmium is 765°C). The metallurgy reactions are (see 29.4):

$$2\,CdS + 3\,O_2 = 2\,CdO + 2\,SO_2$$
$$CdO + C = Cd + CO$$
$$CdS + 2\,H^+ = Cd^{++} + H_2S$$
$$Zn + Cd^{++} = Zn^{++} + Cd$$

29.12 Properties (see Table 29.1). Cadmium has an attractive color and is relatively inactive.

29.13 Uses. The chief uses of cadmium are in cadmium plating (75%), as a component of bearing metals, solders, and fusible alloys (22%), and in the manufacture of CdS. Cadmium adheres firmly to iron, does not rupture easily when the base metal is bent, is resistant to corrosion, has an attractive appearance, is easily applied in the form of a molten spray or by electrodeposition, and serves as an excellent base for electroplating with chromium, nickel, silver, and other metals. For these reasons it is a popular and valuable plating material.

An interesting use of cadmium is in the form of control rods in nuclear reactors. This use depends upon its great capacity for absorbing neutrons. The reaction in the pile is slowed down by increasing the cadmium metal surface, and is speeded up by decreasing the surface. In practice this is accomplished by pushing in or pulling out cadmium rods.

Cadmium sulfide is used as a yellow paint pigment.

29.14 Reactions (see 29.11)

1. $Cd = Cd^{++} + 2e$; $E^\circ = 0.403$ volt.
2. Solution of Cd in HNO_3.

$$3\,Cd + 2\,NO_3^- + 8\,H^+ = 3\,Cd^{++} + 2\,NO + 4\,H_2O$$

3. Reaction of Cd with dilute nonoxidizing acids.

$$Cd + 2\,H^+ = Cd^{++} + H_2$$

4. Precipitation of CdS. This reaction occurs in the separation and identification of cadmium.

$$Cd^{++} + H_2S = \mathbf{CdS}\ (\text{yellow}) + 2\,H^+$$

5. Solution of CdS in HNO_3.

$$3\,\mathbf{CdS} + 2\,NO_3^- + 8\,H^+ = 3\,Cd^{++} + 2\,NO + 3\,S + 4\,H_2O$$

6. Formation of complex ions.

$$\mathbf{Cd(OH)_2} + 4\,NH_3 = Cd(NH_3)_4^{++} + 2\,OH^-$$
$$Cd(NH_3)_4^{++} + 4\,CN^- = Cd(CN)_4^{--} + 4\,NH_3$$

Questions

1. For each of the metals cadmium and zinc: (a) give the name and formula of an important ore; (b) describe briefly how the metal is prepared from its ore; (c) list the important uses of the metal and the properties upon which these uses depend; (d) list important commercial compounds and a use for each; (e) indicate, by equations, how its cation can be identified.

2. Explain, in detail, with necessary equations, what happens when each of the following delivers current: (a) the dry battery; (b) the Daniell cell.

3. Show, by balanced net equations, what takes place: (a) when $Zn(OH)_2$ dissolves in sodium hydroxide solution; (b) when $Cd(OH)_2$ dissolves in ammonium hydroxide; (c) when zinc dissolves in sodium hydroxide solution.

CHAPTER 30

Aluminum

30.1 Importance of aluminum. Aluminum is the third most abundant element in the earth's crust, ranking next to oxygen and silicon. It is one of our best structural metals, ranking second only to iron in this respect. Its siliceous compounds, clay, kaolin, and the feldspars are essential raw materials for the preparation of our most widely used synthetic structural products, cement, brick, and tile. Its oxide, which is one of our outstanding industrial abrasives, is also one of our most versatile industrial catalysts. Because of the large use of aluminumware in the home, it is one of the metals with which most people are familiar. It is the most important element in group III and is the only element in that group that will be considered in detail.

Its position in group IIIA is singular. The element of lower atomic number, boron, is a nonmetal. The elements of higher atomic number are definitely metallic, forming basic hydroxides. Aluminum is thus on the borderline between the metals and nonmetals, and as such, its hydroxide is amphoteric. That it borders on the nonmetallic is indicated further by the fact that its chloride has a low melting point (about 190°C at $2\frac{1}{2}$ atm), has a polymeric formula, Al_2Cl_6, and in the molten state is not a good conductor of electricity. It forms Al^{+++} ions and has only one oxidation state of importance, +3; both of these facts are indicative of its character as a metal.

30.2 Smelter production in tons (1950): World, 1,630,000; U.S., 718,600; Canada, 392,000; U.S.S.R., 209,000; France, 67,000; Norway, 51,000. U.S. consumption, 898,000. 1939 U.S. production 148,400. 1952 U.S. smelter production 937,000. The production and use of aluminum have had a more rapid increase than those of any other metal.

30.3 Occurrence. The most important aluminum minerals are bauxite, $Al_2O_3 \cdot H_2O$ (chief ore); cryolite, Na_3AlF_6; orthoclase feldspar, $KAlSi_3O_8$; corundum, Al_2O_3; emery, Al_2O_3; kaolin, $Al_2Si_2(OH)_4O_5$; and clay (impure kaolin).

30.4 Metallurgy. Aluminum is so reactive and its oxide is so stable that reduction of Al_2O_3 by C or CO is not feasible. Since it is so active

that it reacts with water, electrodeposition of the metal from its water solution will not work. Its melted chloride is a very poor conductor and its oxide melts at the prohibitive temperature of 2045°C; therefore electrolysis of its fused compounds cannot be used as a method of preparation. The alternative, which is the method universally employed for preparing aluminum from its ores, is to electrolyze a solution of its compound in some solvent other than water. The solvent is melted cryolite (Na_3AlF_6) or a synthetic mixture of NaF, AlF_3, and CaF_2 similar to cryolite. The compound that is dissolved in this molten solvent is purified Al_2O_3. The source of this Al_2O_3 is bauxite, $Al_2O_3 \cdot H_2O$.

The crude bauxite is purified by digestion with sodium hydroxide. This dissolves the amphoteric oxide Al_2O_3 to give a solution of the aluminate ion $Al(OH)_4^-$, but does not effect the basic oxide impurities such as Fe_2O_3.

$$Al_2O_3 + 2\,OH^- + 3\,H_2O = 2\,Al(OH)_4^- \text{ (aluminate ion)}$$

Pure $Al(OH)_3$ can be precipitated from this $Al(OH)_4^-$ solution by treatment with a weak acid.

$$Al(OH)_4^- + H^+ = Al(OH)_3 + H_2O$$

This $Al(OH)_3$ is filtered, washed, and dried, and is then heated to a high temperature to yield pure Al_2O_3.

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

The purified Al_2O_3 is then dissolved in molten Na_3AlF_6 in a carbon-lined electrolysis tank fitted with carbon anodes (positive electrodes) (see Figure 30.1). The tank itself functions as the cathode (negative electrode).

In the electrolysis process, the aluminum ion is attracted to the negative electrode where it picks up 3 electrons and deposits as elemental aluminum; the molten aluminum settles to the bottom of the

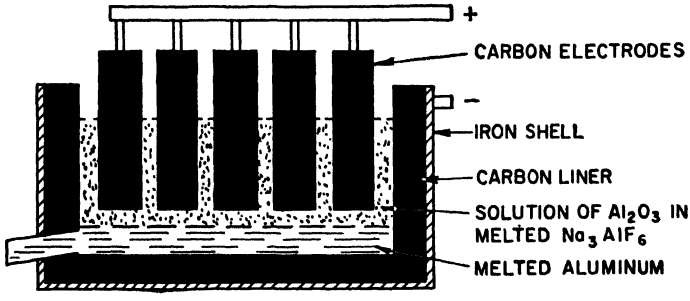


Figure 30.1. The Hall process for the preparation of aluminum.

tank. Oxygen collects at the carbon anode; some of it escapes as O_2 gas but a large part of it reacts with the carbon electrodes, gradually consuming them. The electrolyzed Al_2O_3 is replaced, so the process goes on continually, stopping only while the carbon electrodes are replaced. The melted aluminum is drawn off from the bottom of the tank and is cast into large ingots. The molten aluminum in the tank is protected from air oxidation by the overlying layer of molten Na_3AlF_6.

The process described above is the Hall process, named after the young Oberlin College graduate who devised it in 1886. The relative newness of the Hall process shows what a newcomer aluminum really is among the industrial metals. Before 1886 aluminum was a luxury item; since then it has become one of our cheapest metals.

It should be stated that processes have been worked out for obtaining pure Al_2O_3 from plentiful clay and feldspar, but the high cost will prevent their use as sources of aluminum until our present plentiful world supply of high-grade bauxite ore is depleted.

30.5 Properties. (Since aluminum is the only group IIIA element that will be discussed, the properties of the others are not listed.) At. no. 13; at. wt 26.97; at. diam 2.86 Å; electronic configuration 2, 8, 3; oxidation number 3; density 2.7; mp 660°C; bp 1800°C, ductile, malleable, high tensile strength, good conductor of heat and electricity, silvery-white color, resists corrosion because of formation of protective film of Al_2O_3.

30.6 Uses. Aluminum owes its great value as an industrial metal to its combination of lightness, great tensile strength, high malleability and ductility, high resistance to corrosion, high electric conductivity, and attractive appearance. Its important uses are: aluminum (cast, sheet, wire) and aluminum alloys for aircraft and transportation equipment (38%), building products (20%), power transmission lines (10%), household appliances (8%), cooking utensils (6%), machinery (4%), miscellaneous (14%). A large number of aluminum alloys have been developed; among the more important are duralumin (89.5% Al, 6% Mn, 4% Cu, and 0.5% Mg), magnalium (80–90% Al, 10–20% Mg), and the so-called piston alloys (Al—Cu—Si) and casting alloys (Al—Si—Mg).

30.7 Important compounds and their uses

1. Al_2O_3. It serves as a contact catalyst for a great many industrial chemical processes. Cast into wheels and other shapes it is known as *emery* and is used as an industrial abrasive. Clear, transparent Al_2O_3,

formed by carefully controlled solidification of the fused material, is used for making jeweled bearings for watches and other sensitive instruments, gages of various kinds, thread guides for textile machinery, and synthetic gem stones (sapphires and rubies).

2. $AlCl_3$. It is used as a reactant and catalyst in the synthesis of organic chemical compounds.

3. $Al_2(SO_4)_3$ and aluminum alums. The term *alum* refers to the hydrated double sulfates formed by a monovalent alkali metal (Li, Na, K, Rb, Cs) or ammonium and a trivalent metal (Al, Cr, Fe). The general formula of an alum is $M'_2SO_4 \cdot M'''_2(SO_4)_3 \cdot 24H_2O$. The names and formulas of some specific alums are:

sodium alum, $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
potassium alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
ammonium chrome alum, $(NH_4)_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$
potassium iron alum, $K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$

A double salt ionizes to give the cations and anions of its component salts. For that reason a solution of an aluminum alum behaves like a solution of aluminum sulfate. Because the alums are easily crystallized from solution, and hence are easy to purify, they are commonly used in place of the trivalent metal sulfate.

Aluminum sulfate and alum are used for water purification, as mordants in dyeing, in the manufacture of paper and baking powder, and for other purposes. These uses depend, in general, on the fact that $Al_2(SO_4)_3$, being the salt of a weak base $Al(OH)_3$ and a strong acid H_2SO_4, will (a) hydrolyze to give an acidic reaction; (b) form a flocculent precipitate of $Al(OH)_3$ when treated with a base. The first three uses listed above depend upon the fact that the $Al(OH)_3$ which precipitates will adsorb impurities present in water, will adsorb certain dyes that are not adsorbed by a fabric, and will impregnate the fibers of paper. The use in baking powder depends on the fact that the free acid which is formed on hydrolysis will react with the $NaHCO_3$ present in baking powder to give off CO_2 (see 21.3E).

(a) $$Al^{+++} + 6\,H_2O = Al(H_2O)_5OH^{++} + H^+$$
$$H^+ + HCO_3^- = H_2O + CO_2$$

(b) $$Al^{+++} + 3\,OH^- = \mathbf{Al(OH)_3}$$

4. The use of clay for the manufacture of brick, tile, ceramic ware, and Portland cement has been discussed in Chapter 23.

30.8 Reactions (see 30.4 and 30.7)

1. $Al = Al^{+++} + 3e$; $E^\circ = 1.66$ volts.

2. Reaction of Al with nonoxidizing acids.

$$2\,Al + 6\,H^+ = 2\,Al^{+++} + 3\,H_2$$

One of the interesting chemical properties of aluminum is its apparent failure to react with nitric acid. It is believed that a film of Al_2O_3 forms on the surface as soon as it comes in contact with the acid and prevents further reaction.

3. Reaction of Al with solutions of strong bases.

$$2\,Al + 2\,OH^- + 6\,H_2O = 2\,Al(OH)_4^- + 3\,H_2$$

4. Amphoteric character of $Al(OH)_3$.

$$\mathbf{Al(OH)_3} + 3\,H^+ = Al^{+++} + 3\,H_2O$$
$$\mathbf{Al(OH)_3} + OH^- = Al(OH)_4^-$$

5. Identification of aluminum ions.

$$Al^{+++} + 3\,OH^- = \mathbf{Al(OH)_3}\ \text{(white, flocculent)}$$

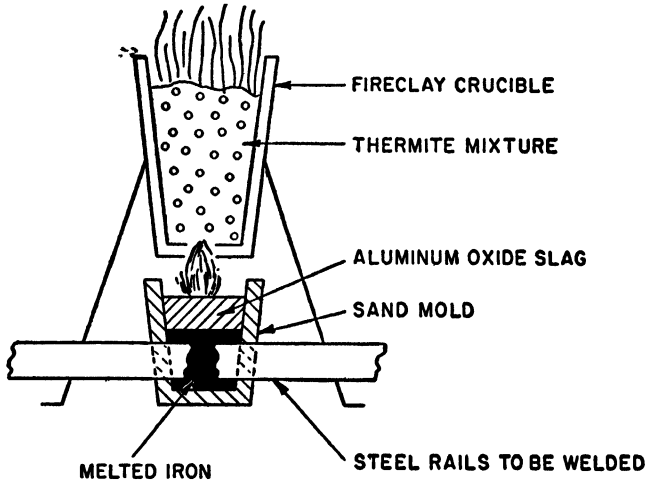


Figure 30.2. Thermite welding. The section to be welded is first surrounded by a sand mold, and a fireclay crucible filled with thermite mixture is then mounted over the mold. A magnesium ribbon wick, lighted with a match, starts the thermite reaction. The heat of the thermite reaction melts the metal plate which covers the hole in the bottom of the crucible, allowing the molten mixture of iron and aluminum oxide to flow into the sand mold. The heavy liquid iron sinks to the bottom of the mold and surrounds the part to be welded, the lighter aluminum oxide slag floats to the top. This type of welding has very limited use.

The $Al(OH)_3$ will adsorb the dye *aluminon*, and will thereby form a red precipitate or *lake*.

6. *The thermite reaction.* Because of the great reactivity of aluminum and the high heat of formation of its oxide (399,090 cal/mole), it will reduce the oxide of a less electropositive metal to the free element, with evolution of sufficient heat to raise the temperature of the element above its melting point. This reaction can therefore be used either to prepare a metal from its oxide ore (see 25.10) or for welding objects together with the molten product element. Thus if a finely divided mixture of Al and Fe_2O_3 is ignited, the reaction

$$Fe_2O_3 + 2\,Al = 2\,Fe + Al_2O_3$$

will proceed at such a rapid rate and with the evolution of so much heat (202,590 cal/mole of Al_2O_3 formed) that the temperature will rise to about 2500°C. At this temperature, metals and alloys will be melted and combustible material will be ignited. The reaction, accordingly, has been used for (a) sabotaging or destroying military installations and equipment by thermite bombs; (b) starting fires by thermite bombs; (c) welding together large sections of metal or mending broken metal castings as in thermite welding (see Figure 30.2).

Questions

1. Outline the process by which aluminum is prepared from crude bauxite.

2. Show, by a series of equations, the amphoteric behavior of $Al(OH)_3$.

3. Account for the fact that a solution of $AlCl_3$ in water shows an acidic reaction.

4. List the important uses of aluminum and the properties upon which these uses depend.

5. Show, by a series of equations, how pure Al_2O_3 can be obtained from a mixture of Fe_2O_3 and Al_2O_3.

6. Give the detailed electronic configuration of the aluminum atom.

CHAPTER 31

Chromium

31.1 The importance of chromium. Chromium is well known to the layman because of its wide use in the chromium-plated parts of automobiles and electrical appliances. If to the millions of tons of chromium-plated ware we add the tremendous quantities of chrome steels of all kinds, numerous other chromium alloys, chromate paint pigments, and chrome-tanned leather, we realize that chromium is another of our important industrial metals. Although molybdenum and tungsten, which fall in group VIB with chromium are, like chromium, essential components of many of the special steels and other alloys that are used in the construction of modern tools and machines, they will not be discussed in detail. Their physical properties, electronic configurations, and oxidation states are, however, given in Table 31.1.

TABLE 31.1

PROPERTIES OF THE GROUP VIB ELEMENTS

Element	Period	At. no.	At. wt	At. diam, Å	Configuration	Oxidation states	Density g/cc	Mp °C	Bp °C	Color
Chromium Cr	4	24	52.01	2.50	2, 8, 13, 1	2, 3, 6	7.1	1615	2200	bluish white
Molybdenum Mo	5	42	95.95	2.72	2, 8, 18, 13, 1	2, 3, 4, 5, 6	10.2	2620	3700	bluish gray
Tungsten W	6	74	183.9	2.74	2, 8, 18, 32, 12, 2	2, 3, 4, 5, 6	19.3	3370	5900	bluish gray

31.2 Mine production of chromite ore containing approximately 44% Cr_2O_3, in tons (1950). (Because only a small amount of pure chromium is prepared from its ores, and because our chromium imports are all in the form of ore, the production figures are given in terms of the ore rather than the metal.) World, 2,530,000; U.S.S.R., 550,000; Union of South Africa, 436,000; Turkey, 385,000; Southern Rhodesia, 320,000; Philippines, 275,000; Cuba, 129,000; U.S. 408. U.S. imports, 1,303,713. U.S. consumption, 980,369. 1952 U.S. production

about 20,000 (38% Cr_2O_3). It is obvious from these figures that we are dependent upon the rest of the world for this important metal.

31.3 Occurrence. Chromite, $Fe(CrO_2)_2$, is the most important ore.

31.4 Metallurgy

1. Reduction of pure Cr_2O_3 by Al.

$$Cr_2O_3 + 2\,Al = 2\,Cr + Al_2O_3$$

The ore is first fused with Na_2CO_3 and then digested with NaOH solution. This dissolves the chromium oxide.

$$FeO \cdot Cr_2O_3 + 2\,OH^- + 3\,H_2O = 2\,Cr(OH)_4^- + FeO$$

The solution of $Cr(OH)_4^-$ is filtered and then treated with dilute acid, which precipitates pure $Cr(OH)_3$. This $Cr(OH)_3$ is dried and thermally decomposed to give pure Cr_2O_3.

$$Cr(OH)_4^- + H^+ = \mathbf{Cr(OH)_3} + H_2O$$
$$2\,Cr(OH)_3 = Cr_2O_3 + 3\,H_2O$$

2. Reduction of chromite by carbon to give an alloy of iron and chromium called *ferrochrome*. Since about 85% of the chromium is used for the manufacture of chrome steel, and since there is no need in this use of chromium to separate the chromium from the iron, most of the chromium ore is subjected to carbon reduction.

$$Fe(CrO_2)_2 + 4\,C = Fe{-}2Cr + 4\,CO$$

3. Air oxidation of chromite ore in the presence of Na_2CO_3 to give Na_2CrO_4. Chromium is then electrodeposited from a solution of this Na_2CrO_4. This method is becoming increasingly important.

$$4\,Fe(CrO_2)_2 + 7\,O_2 + 8\,Na_2CO_3 = 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2$$

31.5 Properties (see Table 31.1). Attractive appearance; very hard; resists corrosion because it becomes passive in air; typical transition metal in that its compounds are colored, its cation forms many complex ions, it exists in several oxidation states, and its highest oxide is acidic.

31.6 Uses. About 85% of the chromium prepared in the United States is used for manufacture of chrome steels of various kinds and alloys containing iron and chromium. The remaining 15% is used for preparation of nonferrous alloys such as stellite (Cr—Co—W) and vitallium (Cr—Co) and for manufacture of chromium compounds for

use in chromium plating, leather tanning, and manufacture of paints and other substances.

31.7 Important commercial compounds and their uses

1. CrO_3. It is used as an electrolyte in chromium plating baths and as an oxidizing agent in organic synthesis.

2. $Cr_2(SO_4)_3$. It is a component of chromium plating baths and is used for tanning and dyeing leather.

3. $Na_2Cr_2O_7$. It is used in leather tanning. The reactions that take place in the tanning of leather are very complex. The $Cr_2O_7^{--}$ ion undoubtedly oxidizes some of the organic material in the leather. The Cr_2O_3 which is formed in the process remains in the pores of the leather and gives it desirable physical properties.

4. $PbCrO_4$, $CdCrO_4$, $ZnCrO_4$, and $BaCrO_4$. They serve as yellow paint pigments.

31.8 Reactions (see 31.4)

1. $Cr = Cr^{+++} + 3e$; $E^\circ = 0.740$ volt. Chromium is a reactive metal.

2. Reaction of chromium with dilute nonoxidizing acids.

$$2\,Cr + 6\,H^+ = 2\,Cr^{+++} + 3\,H_2$$

3. Reaction of chromium with nitric acid.

$$Cr + NO_3^- + 4\,H^+ = Cr^{+++} + NO + H_2O$$

4. Amphoteric character of $Cr(OH)_3$. This reaction is commonly used in the qualitative separation and identification of chromium.

$$\mathbf{Cr(OH)_3} + 3\,H^+ = Cr^{+++} + 3\,H_2O$$

$$\mathbf{Cr(OH)_3} + OH^- = Cr(OH)_4^- \text{ (tetrahydroxochromate(III) ion)}$$

5. Oxidation of chromium(III) to chromium(VI) in alkaline solution. This is an important reaction in the qualitative separation and identification of chromium.

$$2\,Cr(OH)_4^- \text{ (green)} + 3\,H_2O_2 + 2\,OH^- = 2\,CrO_4^{--} \text{ (yellow)} + 8\,H_2O$$

6. Conversion of chromate ion to dichromate ion in acid solution. This is a convenient identification reaction for chromates.

$$2\,CrO_4^{--} \text{ (yellow)} + 2\,H^+ \rightleftarrows Cr_2O_7^{--} \text{ (orange)} + H_2O$$

7. Conversion of dichromate ion to chromate ion in alkaline solution.

$$Cr_2O_7^{--} \text{ (orange)} + 2\,OH^- \rightleftarrows 2\,CrO_4^{--} \text{ (yellow)} + H_2O$$

8. Commercial preparation of CrO_3 by dehydration of $H_2Cr_2O_7$.

$$2\,Na_2CrO_4 + 2\,H_2SO_4 = 2\,Na_2SO_4 + H_2Cr_2O_7 + H_2O$$
$$H_2Cr_2O_7 + H_2SO_4 = 2\,CrO_3 + H_2SO_4 \cdot H_2O$$

9. Reduction of chromates and dichromates. This emphasizes the oxidizing power of chromium (VI) compounds. It should be noted that in the chromate and dichromate ions, chromium behaves as a nonmetal in that its oxide is acidic. Since these ions contain chromium in its high oxidation state, they illustrate the fact that the high-oxidation-state compounds of an element can function as oxidizing agents.

$$Cr_2O_7^{--} + 3\,SO_3^{--} + 14\,H^+ = 2\,Cr^{+++} + 3\,SO_4^{--} + 7\,H_2O$$
$$2\,CrO_4^{--} + 3\,Sn(OH)_4^{--} + 8\,H_2O = 2\,Cr(OH)_4^- + 3\,Sn(OH)_6^{--} + 2\,OH^-$$

Chromates and dichromates are fairly strong oxidizing agents (see table of oxidation potentials, page 380).

10. Oxidation of compounds by CrO_3.

$$CH_3OH + 2\,CrO_3 = Cr_2O_3 + CO_2 + 2\,H_2O$$

11. Self-oxidation of $(NH_4)_2Cr_2O_7$. The nitrogen is oxidized while the chromium is reduced. Heat is necessary to initiate the reaction.

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4\,H_2O$$

12. Identification of the chromate ion.

$2\,Ag^+ + CrO_4^{--} =$ **Ag_2CrO_4** (red; soluble in HNO_3) (see 26.13–6)

$Ba^{++} + CrO_4^{--} =$ **$BaCrO_4$** (yellow; soluble in HCl or HNO_3)

$2\,CrO_4^{--}$ (yellow) $+ 2\,H^+$ (from dilute HNO_3) $\rightleftarrows Cr_2O_7^{--}$ (orange) $+ H_2O$

$Cr_2O_7^{--} + 4\,H_2O_2 + 2\,H^+ = 2\,CrO_5$ (blue) $+ 5\,H_2O$

Questions

1. Outline a method for preparing pure chromium from chromite ore.

2. Give three important commercial uses of chromium and give the properties upon which these uses depend.

3. Point out the properties of chromium, the chromium atom, and the ions formed by chromium which identify it as a typical transition element.

4. Give the detailed electronic structure of the chromium atom.

5. Account for the fact that chromium forms Cr^{+++} and CrO_4^{--} ions.

6. Account for the fact that CrO_4^{--} and $Cr_2O_7^{--}$ are oxidizing agents, while Cr^{++} is a powerful reducing agent.

7. Show by equations how $BaCrO_4$, $CdCrO_4$, $PbCrO_4$, and $ZnCrO_4$, for use as paint pigments, can be prepared from chromite ore.

8. Assuming a current efficiency of 70%, calculate how many coulombs of electricity would be required to deposit 60 g of chromium from a solution of chromium sulfate.

CHAPTER 32

Manganese

32.1 Importance of manganese. The quantity of steel being produced is, we have learned, an index to a nation's industrial well-being. The United States produces annually close to 100 million tons of steel. To produce these 100 million tons requires a minimum of 750,000 tons of manganese. That fact alone identifies manganese as a metal which is absolutely essential to our economy. The fact that one of its compounds, MnO_2, is a necessary component of the millions of flashlight batteries that are in use further emphasizes its importance.

32.2 Mine production of manganese ore, in tons (1950). Manganese, like chromium, is imported almost entirely in the form of the ore. For that reason the production figures are in terms of the 35% manganese content ore rather than the metal. World, 6,050,000; U.S.S.R., 2,200,000; Union of South Africa, 870,000; Gold Coast, 782,000; India, 746,000; French Morocco, 316,000; Brazil, 178,000; Egypt, 167,000; Japan, 147,000; U.S. 134,000. U.S. imports, 1,834,925. U.S. consumption, 1,925,148. All the U.S. production is from low-grade ores of which we have a good supply.

32.3 Occurrence. The most important manganese ores are pyrolusite, MnO_2; rhodocrosite, $MnCO_3$; braunite, $3\,Mn_2O_3 \cdot MnSiO_3$; hausmanite, Mn_3O_4.

32.4 Metallurgy

1. Reduction of MnO_2 by Al. This method yields carbon-free manganese.

$$3\,MnO_2 + 4\,Al = 3\,Mn + 2\,Al_2O_3$$

2. Reduction of MnO_2, $MnCO_3$, Mn_3O_4, and Mn_2O_3 ores by carbon at high temperatures. If the ores contain oxides of iron, as is commonly the case, the product is an iron-manganese alloy called *ferromanganese.*

$$MnO_2 + 2\,C = Mn + 2\,CO$$

3. Reduction of the oxide ores to MnO with natural gas, leaching of the reduced product with sulfuric acid, and electrolysis of the leach

liquor. This is a relatively new method that is well adapted to the processing of our low-grade ores.

$$2\,MnO_2 + CH_4 = 2\,MnO + 2\,H_2O + C$$
$$MnO + 2\,H^+ = Mn^{++} + H_2O$$
$$Mn^{++} + 2e = Mn$$

32.5 Properties. Atomic no. 25; at. wt 54.93; at. diam 2.36 Å; electron configuration 2, 8, 13, 2; oxidation numbers 2, 3, 4, 6, 7; mp 1260°C; bp 1900°C; density 7.42; reddish-gray, hard, and brittle. Its several oxidation numbers, its colored compounds, and its tendency to form complex ions are in line with the fact that it is a transition element.

32.6 Uses. Practically all the manganese produced in the U.S. is used for preparation of ordinary steel (15 lb/ton), special manganese steels, and nonferrous manganese alloys. Manganese bronze (Cu—Mn) is used in making propeller blades for ships, a magnesium-manganese alloy is used for making light-weight parts for all varieties of machinery, while Manganin (Cu—Ni—Mn alloy) is used in making standard electric resistance wire.

32.7 Important commercial compounds and their uses

1. MnO_2. It is used as a reactant in dry batteries (see 25.14 B), as a drier in the manufacture of paints (see 27.7), as an oxidizing agent in manufacture of matches (see 19.8), as a decolorizer in manufacture of glass (see 23.9), and as a catalyst in laboratory preparation of oxygen from $KClO_3$ (see 3.21).

2. $KMnO_4$ (potassium permanganate). It serves as an oxidizing agent in synthesis of some organic compounds, as a disinfectant, as a medicine for treatment of certain skin infections, and as a reagent in analytical chemistry. All its uses are dependent upon its strong oxidizing power.

3. $MnSO_4$. It is a component of many fertilizers and stock foods. Trace amounts of manganese are necessary for the health and development of animals and for the growth of certain fruits and grains.

32.8 Reactions (see 32.4)

1. $Mn = Mn^{++} + 2e$; $E^\circ = 1.18$ volts.
2. Reaction of manganese with dilute nonoxidizing acids.

$$Mn + 2\,H^+ = Mn^{++} + H_2$$

3. Reaction of manganese with nitric acid and with aqua regia.

$$3\,Mn + 2\,NO_3^- + 8\,H^+ = 3\,Mn^{++} + 2\,NO + 4\,H_2O$$
$$3\,Mn + 2\,NO_3^- + 8\,H^+ + 12\,Cl^- = 3\,MnCl_4^{--} + 2\,NO + 4\,H_2O$$

4. Oxidation of $Mn(OH)_2$ by air in alkaline solution.

$$4\,\mathbf{Mn(OH)_2} + O_2\ (\text{air}) = 2\,\mathbf{Mn_2O_3}\ (\text{dark brown}) + 4\,H_2O$$
$$2\,\mathbf{Mn_2O_3} + O_2 = 4\,\mathbf{MnO_2}\ (\text{black})$$

Because of the ease with which this reaction takes place, the white precipitate of $Mn(OH)_2$ which is formed when a solution of Mn^{++} ions is treated with a base quickly turns brown.

5. Oxidation of $Mn(OH)_2$ by H_2O_2. This reaction occurs in a method for qualitative separation and detection of manganese.

$$\mathbf{Mn(OH)_2}\ (\text{white}) + H_2O_2 = \mathbf{MnO_2}\ (\text{black}) + 2\,H_2O$$

6. Precipitation of MnS in qualitative analysis.

$$Mn^{++} + S^{--} = \mathbf{MnS}\ (\text{tan})$$

7. Oxidation by MnO_2. This illustrates the rule that the higher-oxidation-state compounds of an element can function as oxidizing agents.

$$MnO_2 + 2\,Cl^- + 4\,H^+ = Mn^{++} + Cl_2 + 2\,H_2O$$

8. Oxidation by permanganate ion in acid solution; Mn^{++} ions are formed.

$$MnO_4^- + 5\,Fe^{++} + 8\,H^+ = Mn^{++} + 5\,Fe^{+++} + 4\,H_2O$$

The presence of Mn in the MnO_4^- ion illustrates the rule that as the oxidation state of an element increases, it becomes more nonmetallic in its behavior, its oxides being acidic in character. Potassium permanganate is the salt of permanganic acid, $HMnO_4$. The acid anhydride of $HMnO_4$ is Mn_2O_7.

Because the MnO_4^- ion has a characteristic violet color, while the Mn^{++} ion is practically colorless, the end point of the reaction, that is, the point when the MnO_4^- is consumed, is easy to detect. For that reason, a solution of $KMnO_4$ is widely used as a titrating reagent in analytical chemistry.

All the common reducing compounds will reduce MnO_4^- in acid solution. (See table of oxidation potentials, page 380.)

9. Oxidation by permanganate ion in alkaline or neutral solution. The product will be either MnO_2 or MnO_4^{--} (manganate ion) depending upon the exact alkalinity and the strength of the reducing agent (see Table 20.2, page 381).

$$2\,MnO_4^- + 3\,Sn(OH)_4^{--} + 4\,H_2O = 2\,\mathbf{MnO_2} + 3\,Sn(OH)_6^{--} + 2\,OH^-$$

$$2\,MnO_4^- + 2\,I^- = 2\,MnO_4^{--}\ (\text{green}) + I_2$$

10. Oxidation of Mn^{++} ions to MnO_4^-. This is a means of detecting the presence of Mn^{++} ions. Reducing agents must be absent otherwise the MnO_4^- will be reduced.

$$2\,Mn^{++} + 5\,HBiO_3 + 9\,H^+\ (\text{dilute } HNO_3) = 2\,MnO_4^- + 5\,Bi^{+++} + 7\,H_2O$$

11. Commercial preparation of manganates and permangantes. A mixture of MnO_2 and Na_2CO_3 is fused in air.

$$2\,MnO_2\ (\text{pyrolusite}) + 2\,Na_2CO_3 + O_2\ (\text{air}) = 2\,Na_2MnO_4\ (\text{green}) + 2\,CO_2$$

The manganate can then be converted to permanganate by oxidation in solution with ozone.

$$2\,MnO_4^{--} + O_3 + H_2O = 2\,MnO_4^- + O_2 + 2\,OH^-$$

The manganate ion is stable only in alkaline solution. If its solution is made neutral or acidic a *disproportionation* reaction takes place in which some of the MnO_4^{--} is oxidized to MnO_4^- while some of it is reduced to MnO_2.

$$3\,MnO_4^{--} + 2\,H_2O = 2\,MnO_4^- + MnO_2 + 4\,OH^-$$

This latter reaction is utilized in the manufacture of permanganates.

Questions

1. Outline a method for preparing pure manganese from an ore.

2. List the important uses of manganese.

3. List the commercial uses of two manganese compounds.

4. Give the formulas for compounds or ions in which manganese has oxidation numbers of 2, 3, 4, 6, and 7, respectively. Involve each compound or ion as a reactant in an oxidation-reduction reaction.

5. Show, by illustrative reactions involving different reducing agents, the difference in behavior of the MnO_4^- ion when it reacts in acid and alkaline solution.

6. Show by equations how Na_2MnO_4 and $NaMnO_4$ can be prepared from pyrolusite ore.

7. Point out the properties that identify manganese as a transition element.

CHAPTER 33

Iron, Cobalt, Nickel

33.1 The iron family. From the standpoint of their relative positions in the periodic table, iron, cobalt, and nickel are uniquely different from any other group of elements considered so far. They all fall in period 4, they have consecutive atomic numbers, and as indicated in Table 33.1, their physical properties are very similar. The lower density and higher melting point of iron are distinctive, as is the oxidation state of 4 rather than 3 for nickel. It is interesting to know that iron is more than 2000 times as plentiful in the earth's crust as cobalt and more than 600 times as plentiful as nickel.

TABLE 33.1

PROPERTIES OF IRON, COBALT, AND NICKEL

Element	Period	At. no.	At. wt	At. diam, Å	Electron configuration	Stable oxid. states	Mp °C	Bp °C	Density	Color
Iron	4	26	55.85	2.54	2, 8, 14, 2	2, 3	1535	3000	7.86	silver-white
Cobalt	4	27	58.94	2.50	2, 8, 15, 2	2, 3	1480	3000	8.9	silver-white
Nickel	4	28	58.69	2.48	2, 8, 16, 2	2, 4	1452	2900	8.9	silver-white

Iron

33.2 The importance of iron. The United States uses up annually about 17 times as many tons of iron as all the rest of the metals put together. Ours is an age of technology and machines, and these machines are either made from iron and steel or are made by machines that are made from iron and steel. Development of modern alloy steels with their tremendous capacity for withstanding shock and wear has made possible perfection of devices that have doubled, quadrupled, and centupled a man's capacity for doing work, and have given us a standard of living unheard of 50 years ago.

33.3 Production of steel in tons (1950). World 204,600,000; U.S. 96,836,000; U.S.S.R., 29,700,000; Great Britain, 18,210,000; Federal

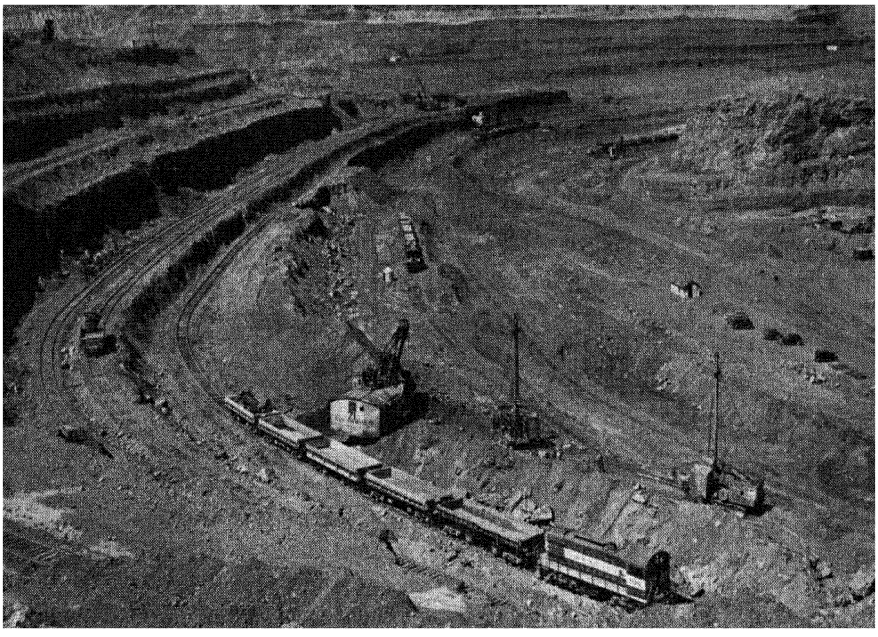


Figure 33.1. The Hull-Rust open pit iron mine, Hibbing, Minnesota. (*Courtesy United States Steel Corporation*)

German Republic, 13,333,000; France, 9,517,000; Japan, 5,333,000; Belgium, 4,167,000; Canada, 3,377,000; Czechoslovakia, 3,010,000; Luxembourg, 2,694,000; Italy, 2,598,000; Saar, 2,086,000; Sweden, 1,582,000; India, 1,581,000. 1952 U.S. production, 101,000,000. 1953 U.S. production, about 113,000,000.

33.4 Occurrence. Hematite, Fe_2O_3; limonite, $Fe_2O_3 \cdot H_2O$; magnetite, Fe_3O_4; siderite, $FeCO_3$; pyrite, FeS_2. Of the 125,739,478 tons of crude iron ore mined in the United States in 1950, 104,392,120 tons or 83.2%

TABLE 33.2

SOURCES OF IRON ORE IN U.S. IN 1950 BY STATES

State	*Tons of ore mined*	*Type of ore*
Minnesota	82,168,368	hematite
Michigan	12,691,101	hematite
Alabama	10,885,487	hematite and brown ore
New York	6,722,422	magnetite
Utah	3,139,926	magnetite
Texas	2,599,723	brown ore
Pennsylvania	1,762,540	magnetite
Wisconsin	1,701,638	hematite
New Jersey	1,090,826	magnetite
Georgia	999,213	brown ore
California	831,445	hematite
Missouri	587,134	hematite
Wyoming	491,906	hematite

was hematite, 12,940,950 tons or 10.2% was magnetite, and 8,406,408 tons or 6.6% was brown ore (limonite and siderite). About 77% of this ore was obtained from open-pit mines, while about 23% was mined underground (see Figure 33.1). The states which yielded this ore are listed in Table 33.2.

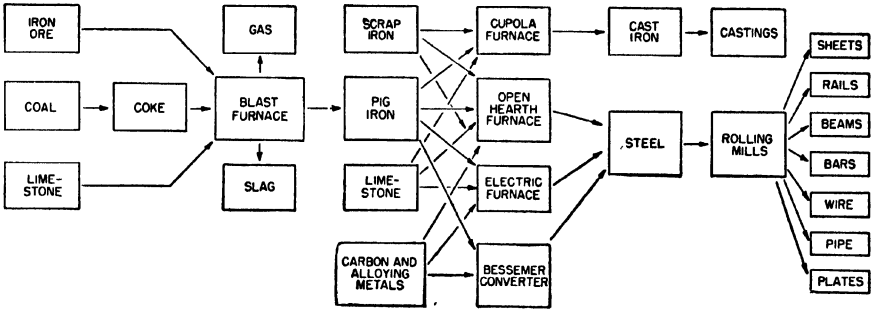


Figure 33.2. Flow sheet showing steps and materials used in manufacture of cast iron and steel from iron ore.

A process has recently been developed whereby low-grade *taconite* ores containing magnetite (Fe_3O_4) can be concentrated by magnetic separation (see 25.10). It has been estimated that this process increases our reserve of utilizable iron ore by several billion tons.

33.5 Metallurgy. The metallurgy of iron consists of (A) reduction of iron ore to pig iron in the blast furnace, and (B) conversion of pig iron to cast iron and steel in cupola, open-hearth, Bessemer, or electric furnaces (see Figure 33.2).

A. *Conversion of Iron Ore to Pig Iron.* A mixture of ore, coke, and limestone is fed into the top of the blast furnace (Figures 33.3 and 33.4). Hot air blown in at the bottom oxidizes the coke in a reaction which generates the heat necessary to bring about the other reactions and keep the products of these reactions in a molten state.

$$C + O_2 = CO_2 + \text{heat}$$

As the CO_2 gas rises in the furnace, it is reduced to CO by the overlying layers of hot coke.

$$CO_2 + C = 2\,CO$$

This CO and the unburned coke are the reducing agents which convert the Fe_2O_3 to iron. The net equations for the reactions are

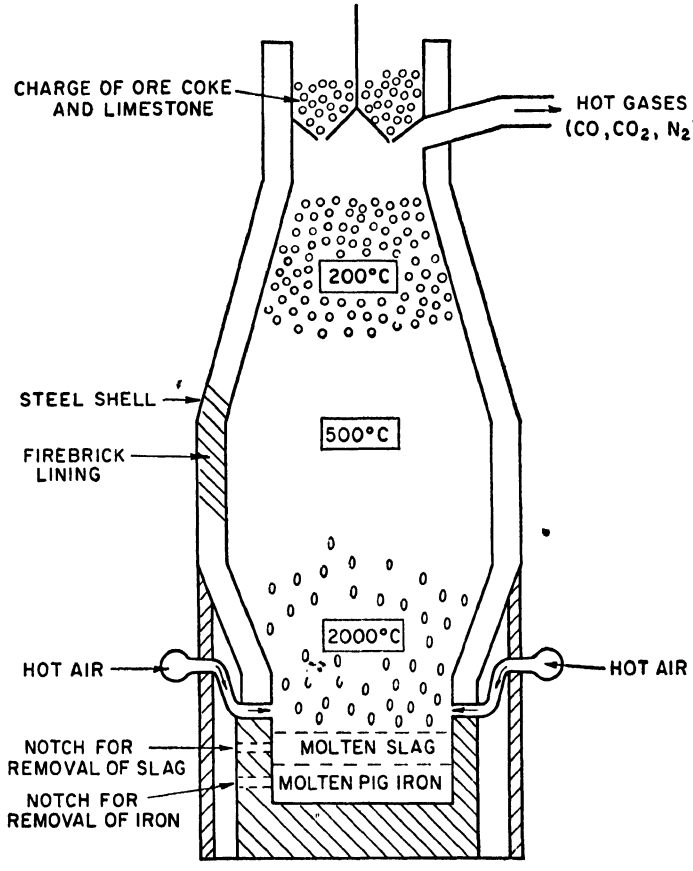


Figure 33.3. Manufacture of pig iron in the blast furnace.

$$Fe_2O_3 + 3\,CO = 2\,Fe + 3\,CO_2$$
$$Fe_2O_3 + 3\,C = 2\,Fe + 3\,CO$$

The dense molten *pig iron* that is formed settles to the bottom of the furnace, where it is drawn off at regular intervals.

The ores that are processed generally contain sand, clay, and silicate rocks as impurities. These are removed when they react with the limestone *flux* to form a mixture of low-melting compounds referred to as *slag*. Some typical reactions involved in this slag-formation process are

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2$$
$$8\,CaCO_3 + 2\,KAlSi_3O_8 = 6\,CaSiO_3 + 2\,Ca(AlO_2)_2 + K_2CO_3 + 7\,CO_2$$

The molten slag flows to the bottom of the furnace, but being of lower density, it floats on top of the iron.

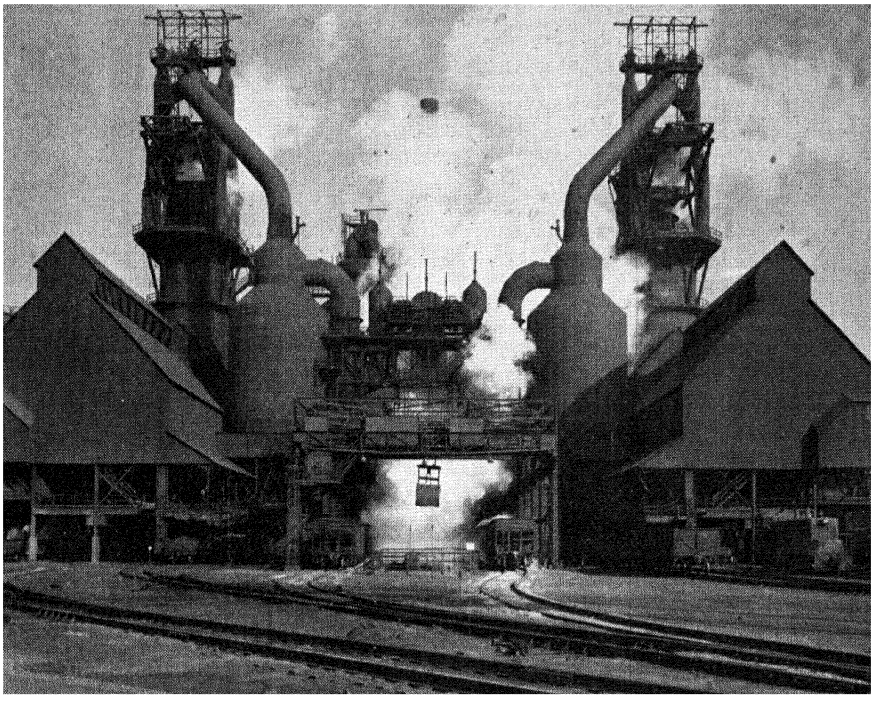


Figure 33.4. Twin blast furnaces. (*Courtesy United States Steel Corporation*)

The hot gases that escape from the top of the furnace are a mixture of N_2, CO_2, CO, H_2, and steam. They are first circulated through a heat exchanger, where they help heat the air that is blown into the furnace. Being combustible due to their CO and H_2 content, they are then burned in stoves which further heat up the air blast and also provide the power and light necessary for operation of the furnace.

The slag that is drawn off at regular intervals and allowed to solidify is, depending upon its composition, used as road-building aggregate, as a fertilizer (if its content of potassium and/or phosphorus is sufficiently high), or as a source of Portland cement (if it contains the correct per cent of calcium silicate, and aluminate).

B. *Conversion of Pig Iron to Cast Iron and Steel.* The pig iron contains such a high per cent of impurities (S, C, Si, P, and Mn in the form of compounds) that in the solid form it is too brittle to be useful for making anything but castings of various kinds. Accordingly, the greater per cent of it is transferred to cupola, open-hearth, Bessemer, or electric furnaces, where it is converted into high-grade cast iron, malleable iron, or steel. The detailed processes for producing these products are quite involved. In brief, they are carried out as follows.

1. *Manufacture of cast iron and malleable iron.* The molten pig iron drawn from the blast furnace is transferred to what is called a cupola furnace, where it is mixed with anywhere from 150% to 180% of its

weight of scrap iron and a small amount of limestone flux. A hot blast of air and burning gas keeps the mass molten and oxidizes part of the impurities present. The limestone reacts with these oxidation products to form a slag which can be skimmed off. The cast iron that is produced contains from 1.5 to 3.5% of carbon, about 1% silicon, and smaller amounts of sulfur, phosphorus, and manganese. When this cast iron is subjected to properly controlled heating and cooling, it yields a relatively soft, malleable product called malleable iron.

2. *Manufacture of steel.* The conversion of pig iron to steel consists essentially of two steps: (a) removal of practically all the impurities by the oxidizing action of hot air and iron rust (Fe_2O_3), the fluxing action of $CaCO_3$, and the reducing action of silicon and aluminum; (b) addition to this purified iron of enough carbon and alloying metals to give steel of the desired quality. These two steps are carried out in either an open-hearth furnace, a Bessemer converter, or an electric furnace.

The open-hearth process. In the open-hearth process (see Figure 33.5) the molten pig iron is mixed with about 85% of its weight of scrap iron, some high-grade iron ore, and a liberal amount of limestone, the total charge ranging in weight with the size of the furnace from 50 to about 500 tons. A blast of burning gas, oil, or powdered coal keeps the mass molten during the 8 to 12 hours required for processing each batch.

The iron oxide oxidizes the impurities (C, S, Si, P) to their oxides.

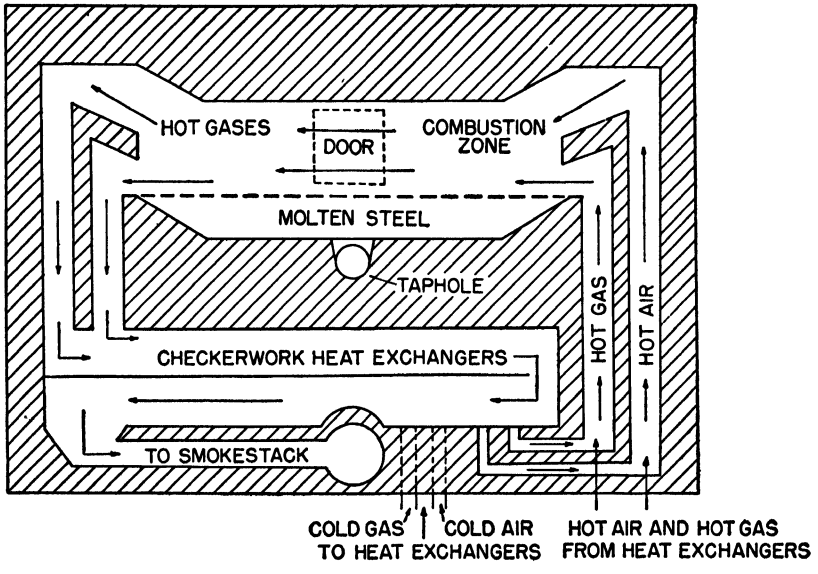


Figure 33.5. Schematic diagram of an open-hearth furnace.

$$Fe_2O_3 + 3\ C\ (S, Si, P) = 2\ Fe + 3\ CO\ (SO_2, SiO_2, P_4O_{10})$$

The CO and SO_2 gases escape, causing the mass to bubble and foam. The SiO_2 and P_4O_{10} react with the $CaCO_3$ to form a slag, which floats to the top and can be drawn off. When the impurities are completely oxidized, enough aluminum or silicon is added to reduce the excess iron oxide to iron. The slag is then all removed, and about 15 pounds of manganese is added to each ton of molten material; it reduces to iron any iron sulfide that may be present and thereby prevents cracking of the steel due to the presence of FeS.

The last step in the process consists in adding exactly the right amount of carbon and alloying metals to give steel of the desired quality.

The Bessemer process. The molten pig iron is run directly from the blast furnace into the top of the egg-shaped crucible (Figure 33.6), and a

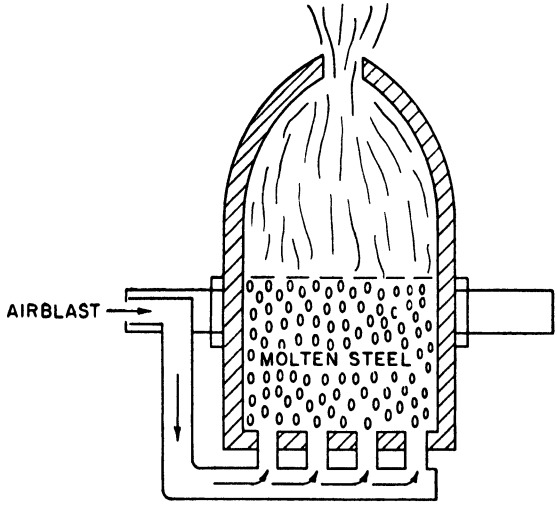


Figure 33.6. A Bessemer converter.

blast of air is blown through the molten mass until the color of the flame shows that the impurities have been oxidized. Scrap iron is often added during the blowing operation to keep the temperature from going too high.

The oxidation requires about 10 minutes, and when it is complete, the amount of carbon necessary to give the desired quality of steel is added.

The Bessemer process has no provision for removing oxides that require fluxing. For that reason it is not satisfactory for treatment of pig iron derived from ore that contains much sulfur, phosphorus, and silicon.

The electric furnace. This is essentially a small open-hearth furnace in which the heat is furnished by electricity instead of by burning fuel. Small-batch preparation of special alloy steels is almost always carried out in electric furnaces.

Of the total of 64,943,118 tons of pig iron that were produced in the United States in 1950, about 3.5% was used directly, without further treatment, for making castings, about 9.3% was converted into cast iron and malleable iron, while about 87.2% was converted into steel.

Of the total of 96,836,075 tons of steel produced in the United States in 1950, about 89% was produced in open-hearth furnaces, about 6.3% in electric furnaces, and only about 4.7% in Bessemer converters.

33.6 The properties of steel. The properties of a piece of steel are determined by:

1. *Its carbon content.* Other things being equal, the hardness of a piece of steel increases as the carbon content increases up to the maximum of about 1.5%. If the carbon content is greater than 1.5% the product is generally referred to as cast iron.

2. *The alloying metals.* A detailed discussion of the specific qualities of the hundreds of steels that are obtained by use of various combinations of the different alloying metals, and of the reason why the specific metal gives the alloy its unique quality, is beyond the scope of this book. However, a general summary of the qualities which the alloying metals impart to steel is given in Table 33.3. It will be noted in this table that the important alloying metals are the high-density small-atomic-diameter transition elements. Since iron itself is a high-density, small-atomic-diameter element, it is reasonable to expect that elements of essentially the same character would be inclined to blend with or intermesh with its crystal structure in such a way as to give the hardness, high density, and rigidity which characterize all the steel alloys.

3. *The heat treatment.* The properties of a piece of steel are affected profoundly by the heat treatment which it receives. To illustrate: if a piece of steel containing 1% carbon is heated to about 1400°C and is then allowed to cool slowly to room temperature, the product is soft and ductile and can easily be bent. If instead of being allowed to cool slowly from 1400°C to room temperature, the original piece of steel is chilled by immersion in cold water or oil, the product is very hard, nonductile, and brittle. If this piece of hard chilled steel is heated all the way up to 1400°C and is then allowed to cool slowly, it will become soft and ductile. If the chilled steel is heated up to some intermediate temperature, say 500°C, and is then allowed to cool slowly, the product will be softer than the original hard piece, but will be harder than the product formed on

TABLE 33.3

TYPICAL STEELS

(Alloy steels generally contain about 0.4% C)

Composition	Distinctive qualities	Typical uses
0.1–0.3% C (low carbon)	relatively soft	wire, rods, strap
0.3–0.8% C (medium carbon)	moderately hard	structural iron, auto frames, bolts, nails
0.8–1.5% C (high carbon)	very hard, brittle	files, knives, axes, drills, chisels
Ni, Ni—Cr, and Ni—Cr—Mo	hard, tough, strong	armor plate, projectiles, crankshafts, truck and engine frames, steam shovels
1.75% Mn	strong, easily machined and worked	farm machinery, road graders
1% Cr	strong, flexible	springs, sawblades
W—Cr—Co—Mo—V	retains hardness at high temperatures	cutting tools, drills
13% Cr; 18% Cr, 1% Ni (stainless steel)	resists corrosion, tough	food-processing machinery, surgical instruments, kitchen utensils
12–15% Si (Duriron)	resists corrosion, brittle	sewer pipe, acid containers
0.1% V	tough	truck, auto and locomotive parts
0.1% Ti	hard, tough, wear-resistant	railroad rails
35% Co	high magnetic strength	magnets
1% Cu	rust-resistant	wire, sheet

slow cooling from 1400°C. The product formed by heating the chilled steel to 600°C and then allowing it to cool to room temperature will be softer than the product formed by heating to 500°C. As a general rule, the higher the temperature to which a piece of chilled steel is heated and then allowed to cool, the greater the amount of hardness that will be removed and the softer the product. A piece of chilled steel that is heated to 800°C, allowed to cool slowly to 600°C, and then quenched (chilled) at 600° will be harder than a piece that is heated to 800°C, allowed to cool slowly to 500°C, and then quenched. Furthermore, a piece of steel that is chilled from 1500°C to room temperature will be

harder than a piece that is chilled from 1200°C or 1000°C. Also, a piece that is chilled from 1200°C to 700°C will not be so hard as a piece that is chilled from 1200°C to 200°C. In other words, *the greater the chilling range, the harder the steel,* and *the greater the slow-cooling range, the softer the steel.* By varying the extent of the chilling range and the cooling range, a 1% carbon steel can be given practically any degree of hardness desired.

The over-all process in which the hardness and brittleness of steel are altered by heat treatment is called *tempering.* The specific process in which a hard steel is softened by heating to some moderately high temperature and cooling slowly is called *annealing.* The presence of alloying metals along with the carbon modifies the net effect of the tempering process; tungsten, for example, causes steel to remain hard in spite of long heating over wide temperature ranges. That means that by varying the per cent of carbon the per cent and identity of the alloying metals, and the heat treatment, it is possible to obtain a steel of practically any desired hardness, brittleness, flexibility, malleability, ductility, and tensile strength.

The changes that take place in the structure of the steel during the heat treatment process are quite complex. Stated briefly and simply, this is essentially what happens: At high temperature the carbon, which exists as the compound Fe_3C, called *cementite,* is dissolved in the iron in what is referred to as a *solid solution.* The solubility of Fe_3C in solid iron decreases as the temperature decreases. That means that when steel is cooled, Fe_3C crystallizes out. If the rate of cooling is slow, the crystallizing Fe_3C has a chance to collect into large crystals; between these crystals there are relatively large areas of practically pure iron. This pure iron is soft, and will accordingly make the piece of steel soft. If the steel is chilled rapidly, the Fe_3C does not have a chance to gather into large crystals, but remains dispersed throughout the mass of nearly pure iron in the form of minute crystals. These crystals interfere with the free slippage of the planes in the iron lattice; essentially, they lock these planes in place. As a result the mass is hard, nonductile, and brittle. Annealing releases the minute Fe_3C crystals and allows them to gather into larger crystals; this produces larger areas of pure iron and thereby reduces the hardness and brittleness. The atoms of the alloying metals can also lock the iron atoms into place, thereby increasing the hardness. A certain combination of elements may give a structure which can be deformed under stress but returns to the original structure when the stress is removed. This is the basis for the use of an alloy containing small percentages of V, Ni, Cr, and Mn in making automobile springs.

Case hardened steel articles are prepared in such a way that the

surface layers have a high carbon content and accordingly become hard and wear-resistant when chilled, while the interior contains a low per cent of carbon and therefore is softer, tougher, and less brittle. This is desirable in such things as automobile axles or engine shafts, which must be strong and tough so as to resist shock, but whose surface must be hard enough to resist wear. The increase in carbon content of the surface is accomplished by heating it in contact with charcoal or some carbon compound.

4. *Mechanical treatment* (cold working). When a piece of cold steel is hammered, rolled, drawn, or otherwise distorted by some kind of physical strain, its hardness and brittleness increase. The failure and breakage of machine parts, bolts, and wire that are subjected to twisting, bending, and pounding are generally caused by this embrittlement. The breaking of a steel wire by bending it back and forth several times is a familiar example. The cold-worked metal can be restored to its original condition by proper heat treatment.

33.7 Important commercial compounds and their uses

1. Fe_2O_3. It is used as a paint body and pigment in the manufacture of the red paint used in steel structures and farm buildings, as an abrasive or rouge in the manufacture of plate glass and the polishing of metal surfaces, and as a pigment in the preparation of red concrete.

2. $FeSO_4$. It is used in water treatment, in the manufacture of blue-black ink, in the dyeing of fabrics, and as a weed killer. Its use in dyeing and water purification depends upon the ease with which it is oxidized in alkaline solution to yield a precipitate of $Fe(OH)_3$.

$$4\,Fe^{++} + 8\,OH^- + O_2 + 2\,H_2O = 4\,Fe(OH)_3$$

This $Fe(OH)_3$ adsorbs impurities in the water and acts as a mordant with certain dyes. Blue-black ink, as it is contained in the bottle, is a solution of $FeSO_4$, tannic acid, and a blue dye. When the ink is exposed to the air, the Fe^{++} ions are oxidized to Fe^{+++}; these iron(III) ions react with the tannic acid to form a permanent black precipitate of iron(III) tannate. The blue dye gives the ink its temporary color until the final black color develops.

$$4\,Fe^{++} + O_2 + 2\,H_2O = 4\,Fe^{+++} + 4\,OH^-$$

$$Fe^{+++} + \text{tannic acid} = \text{ferric tannate (black precipitate)}$$

3. Fe_3O_4. It is used in the thermite mixture (see 30.8).

4. $FeNH_4(C_3H_4OHCOO)_4$, ferric ammonium citrate. It is used in the manufacture of blueprint paper. Blueprint paper is impregnated with ferric ammonium citrate and potassium ferricyanide. On exposure to

light, the ferric ions are reduced to the ferrous state. When the light-exposed paper is soaked in water, the ferrous ions and ferricyanide ions interact to form a blue precipitate, $Fe_3[Fe(CN)_6]_2$. The part of the blueprint paper that was protected from light exposure remains white, since Fe^{+++} ions do not form a precipitate with $Fe(CN)_6^{---}$ ions.

$$Fe^{+++} + \text{light} + e^- = Fe^{++}$$
$$3\,Fe^{++} + 2\,Fe(CN)_6^{---} = \mathbf{Fe_3[Fe(CN)_6]_2}\ \text{(blue)}$$

33.8 Reactions (see 33.5 and 33.7). (Iron has stable common oxidation states of +2 and +3).

1. $Fe = Fe^{++} + 2e$; $E^\circ = 0.44$ volt. Iron is moderately electropositive.

2. Liberation of H_2 by iron from dilute nonoxidizing acids. The fact that Fe^{++} ions rather than Fe^{+++} ions are formed illustrates the rule that in the presence of a reducing agent (H_2, Fe), an element that can exist in more than one oxidation state tends to take a lower state.

$$Fe + 2\,H^+ = Fe^{++} + H_2$$

When the acid is dilute H_2SO_4, as is the case when sheet iron is cleaned (pickled) preparatory to metal plating, hydrated ferrous sulfate (iron(II) sulfate hexahydrate), $FeSO_4 \cdot 6H_2O$, crystallizes out from the solution. This is the commercial method for preparing ferrous sulfate.

3. Reaction of iron with chlorine, nitric acid, aqua regia, and other oxidizing agents to yield iron(III) compounds. In the presence of oxidizing agents the iron goes to its higher oxidation state.

$$2\,Fe + 3\,Cl_2 = 2\,FeCl_3$$
$$Fe + NO_3^- + 4\,H^+ = Fe^{+++} + NO + 2\,H_2O$$
$$Fe + NO_3^- + 4\,H^+ + 4\,Cl^- = FeCl_4^- + NO + 2\,H_2O$$

Iron, in common with all metals except those in groups IA and IIA, forms a complex chloro ion when dissolved in aqua regia.

4. The precipitation of $Fe(OH)_3$. This reaction occurs in the separation and detection of iron.

$$Fe^{+++} + 3\,OH^- = \mathbf{Fe(OH)_3}\ \text{(reddish brown)}$$

5. The precipitation of FeS.

$$Fe^{++} + S^{--} = \mathbf{FeS}\ \text{(black)}$$

6. The oxidation of iron(II) to iron(III). The potential of the reaction, $Fe^{++} = Fe^{+++} + e$, is -0.771 volt. That means that Fe(II) ions will reduce those substances whose oxidation potentials lie below

about −0.8 (see Table 20.1); it means also that the Fe^{+++} ion is a fairly strong oxidizing agent.

$$4\,Fe^{++} + 3\,O_2\ (\text{air}) + 6\,H_2O = 4\,\mathbf{Fe(OH)_3}$$

$$3\,Fe^{++} + NO_3^- + 4\,H^+ = 3\,Fe^{+++} + NO + 2\,H_2O$$

$$3\,Fe^{++} + NO_3^- + 4\,H^+ + 12\,Cl^-\ (\text{aqua regia}) = 3\,FeCl_4^- + NO + 2\,H_2O$$

$$2\,\mathbf{Fe(OH)_2}\ (\text{white}) + H_2O_2 = 2\,\mathbf{Fe(OH)_3}$$

$$5\,Fe^{++} + MnO_4^- + 8\,H^+ = 5\,Fe^{+++} + Mn^{++} + 4\,H_2O$$

This last reaction is important in the quantitative determination of iron. An aliquot portion of a solution whose iron content is to be determined is titrated with a standard solution of MnO_4^- (see 32.8).

$$6\,Fe^{++} + Cr_2O_7^{--} + 14\,H^+ = 6\,Fe^{+++} + 2\,Cr^{+++} + 7\,H_2O$$

This reaction is used for the quantitative determination of iron.

$$Ce^{++++} + Fe^{++} = Ce^{+++} + Fe^{+++}$$

This reaction is widely used for the quantitative determination of iron. (See Table 20.1, page 380, for other common oxidizing agents that will oxidize Fe^{++} to Fe^{+++}.)

7. Reduction of Fe(III) to Fe(II).

$$2\,Fe^{+++} + H_2S = 2\,Fe^{++} + 2\,H^+ + \mathbf{S}$$

This occurs in qualitative analysis when a solution containing Fe^{+++} ions is treated with H_2S to precipitate the sulfides of the metals from acid solution.

$$2\,\mathbf{Fe(OH)_3}\ (\text{reddish brown}) + 3\,S^{--} = 2\,\mathbf{FeS}\ (\text{black}) + S + 6\,OH^-$$

This occurs when H_2S or sulfide ion is added to a precipitate of $Fe(OH)_3$ in qualitative analysis for the cations.

$$2\,Fe^{+++} + 2\,I^- = 2\,Fe^{++} + \mathbf{I_2}$$

This reaction will serve to identify iodides in the presence of bromides and chlorides, since the latter two are not oxidized by Fe^{+++} ion. (Consult Table 20.1, page 380, for other reducing agents that will reduce Fe^{+++} to Fe^{++}.)

8. Formation and reaction of Fe(III) complex ions. The tendency of Fe^{+++} to form complex ions is in line with the fact that iron is a transition metal. Most of these complex ions are colored. As has already been pointed out in Section 14.7, the composition of the complex ion will vary with the concentration of the complexing agent.

$$Fe^{+++} + 6\,SCN^- \rightleftarrows Fe(SCN)_6^{---} \text{ (blood red)}$$

This is a sensitive test for Fe^{+++} ions.

$$Fe^{+++} + 4\,Cl^- \rightleftarrows FeCl_4^- \text{ (yellow)}$$
$$Fe^{+++} + 6\,F^- \rightleftarrows FeF_6^{---} \text{ (colorless)}$$

This reaction is used in qualitative analysis as a means of preventing interference from Fe^{+++} ions when testing for cobalt ions with SCN^- ions; Fe^{+++} ions are tied up as FeF_6^{---} ions.

$$4\,Fe^{+++} + 3\,Fe(CN)_6^{----} = \mathbf{Fe_4[Fe(CN)_6]_3} \text{ (dark blue)}$$

This is a sensitive test for Fe^{+++} ions.

9. Identification of Fe^{+++} ions. (See 8 above.)
10. Identification of Fe^{++} ions.

$$3\,Fe^{++} + 2\,Fe(CN)_6^{----} = \mathbf{Fe_3[Fe(CN)_6]_2} \text{ (dark blue)}$$

11. *Reactions that take place in the atmospheric rusting of iron.* Rusting of iron requires the presence of both moisture and air. If a piece of iron is kept dry, it will not rust in contact with air; if it is kept out of contact with air, it will not rust even though it is in contact with water. This leads to the conclusion that atmospheric rusting is a two-stage process involving first, reaction of iron with water to form $Fe(OH)_2$ and H_2,

$$Fe + H_2O = Fe(OH)_2 + H_2$$

and second, the subsequent oxidation of the $Fe(OH)_2$ to hydrated Fe_2O_3 and the H_2 to H_2O. The hydrated Fe_2O_3 does not stick to the surface of iron the way Al_2O_3 sticks to aluminum, but falls off, thereby exposing new iron to the action of air and moisture. Oxidation of the H_2 to H_2O removes the film of hydrogen gas and keeps the iron exposed to the air and moisture.

$$4\,Fe(OH)_2 + O_2 + H_2O = 2\,Fe_2O_3 \cdot X\,H_2O \text{ (iron rust)}$$
$$2\,H_2 + O_2 = 2\,H_2O$$

If iron can be kept out of contact with air and moisture it will not rust. This is accomplished commercially by coating it with: (a) paint; (b) tin, zinc, cadmium, copper, chromium, and nickel; (c) Fe_3O_4. The hot iron is brought in contact with steam; the following reaction occurs:

$$3\,Fe + 4\,H_2O = Fe_3O_4 + 4\,H_2$$

The Fe_3O_4 adheres firmly to the iron.

12. *Corrosion of iron as a result of galvanic action.* When a piece of iron or steel is brought in contact with a metal or other substance of

lower oxidation potential and the couple is immersed in a solution of an electrolyte, galvanic action takes place (see 25.13). The iron, being more electropositive, corrodes and becomes the negative pole of a battery. The electrolyte solution may contain carbonic acid as in rain water, or various other substances.

If one part of a piece of iron or steel is hammered or drawn or otherwise brought under strain, it becomes more electropositive than the unstrained part. Accordingly, when this piece of iron comes in contact with a solution of an electrolyte, a battery is set up in which the strained portion corrodes and becomes the negative pole. The reactions that take place are

$$Fe = Fe^{++} + 2e; \qquad 2\,H^+ + 2e = H_2$$

The oxygen from the air speeds up the process by removing the hydrogen so that it does not coat the positive pole of the battery. Also, it oxidizes Fe^{++} to iron rust.

$$O_2 + 2\,H_2 = 2\,H_2O$$
$$4\,Fe^{++} + O_2 + 8\,OH^- = 2\,Fe_2O_3 + 4\,H_2O$$

Cobalt

33.9 Mine production, in tons (1950). World, 7800; Belgian Congo, 5660; Northern Rhodesia, 737; French Morocco, 429; U.S., 330; Canada, 312. U.S. consumption, 4142; U.S. imports, 4715. 1952 U.S. mine production, 600.

33.10 Occurrence. Practically all cobalt is associated in low per cent with arsenic, copper, nickel, iron, lead, zinc, or manganese ores. It occurs as cobaltite (CoAsS), and smaltite [$CoAs_2$ and $Co_3(AsO_4)_2$].

33.11 Metallurgy. It is a complex process involving roasting and reduction to form an alloy with the associated metal or metals, followed by chemical or chemical-electrolytic separation.

33.12 Properties (see Table 33.1)

33.13 Uses. The important uses of cobalt are manufacture of magnet alloys (35%), high-temperature, high-strength Co—Cr—W—Mo stellite alloys (27%), nonmagnetic steel alloys (13%), carbide cutting tools (1%), and cobalt oxide and cobalt salts (24%). In the manufacture of carboloy carbide cutting tools, the carbide (usually tungsten carbide) is cemented into a cobalt base.

33.14 Important commercial compounds and their uses

1. CoO. It is used as a blue pigment in the manufacture of ceramics, glass, glazes, enamels, and paints, and as a catalyst in organic chemical reactions.

2. $CoSO_4$ and $CoCO_3$. They serve as reagents for preparation of other cobalt compounds.

33.15 Cobalt-60. The radioactive cobalt isotope with a mass number of 60 is formed when ordinary cobalt metal is bombarded with neutrons in the nuclear reactor.

$$_{27}Co^{59} + {}_0n^1 = {}_{27}Co^{60}$$

Cobalt-60 disintegrates with the emission of beta rays; it has a half-life of about 5 years.

$$_{27}Co^{60} = {}_{28}Ni^{60} + {}_{-1}e^0 \text{ (beta emission)}$$

The beta emission is accompanied by high-intensity gamma radiation. Because of the high intensity of this gamma radiation and the high rate at which it is given off, cobalt-60 can be used in place of radium and radon in research and in medical therapy. Whereas radium costs about \$1000 per curie, the cost of cobalt is less than \$10. Not only is cobalt-60 cheaper than radium, but it is much more convenient to use. Cobalt wire is easy to manipulate; extremely thin wires can readily be inserted into regions of the body that would be practically inaccessible to vials of radon gas. Since the cobalt-60 content, and hence the total activity in curies, of a piece of cobalt metal are proportional to the length of time it is bombarded by neutrons, it is possible to prepare specimens with activity ranging all the way from a few millicuries to one or more kilocuries. A doctor or scientist can thus have radioactivity tailor-made to suit the particular use to which it is put. Furthermore, the same piece of cobalt can be used over and over for several years. It should be noted that more than a year of neutron bombardment in the type of nuclear reactor available today is necessary to bring the activity of a piece of cobalt up to a value of one kilocurie.

33.16 Reactions. Cobalt has a principal oxidation state of +2; the +3 state is not very stable except in complex ions.

1. $Co = Co^{++} + 2e$; $E^\circ = 0.277$ volt.

2. Reaction of cobalt with dilute nonoxidizing acids.

$$Co + 2\,H^+ = Co^{++} + H_2 \text{ (slow reaction)}$$

3. Reaction of cobalt with nitric acid and aqua regia.

$$3\,Co + 2\,NO_3^- + 8\,H^+ = 3\,Co^{++} + 2\,NO + 4\,H_2O$$

$$3\,Co + 2\,NO_3^- + 8\,H^+ + 12\,Cl^- = 3\,CoCl_4^{--} + 2\,NO + 4\,H_2O$$

4. Precipitation of $Co(OH)_2$.

$$Co^{++} + 2\,OH^- = \mathbf{Co(OH)_2}\ \text{(blue)}$$

5. Formation of the complex cobaltamine ion. The Co(II) is readily oxidized to Co(III) in alkaline solution. Cobalt forms a great many complex ions. This is in line with the fact that it is a transition metal.

$$4\,Co(OH)_2 + O_2\ (air) + 2\,H_2O + 24\,NH_3 = 4\,Co(NH_3)_6^{+++} + 12\,OH^-$$

6. Precipitation of CoS in alkaline solution. The oxidation state of +3 is readily reduced to +2.

$$2\,Co(NH_3)_6^{+++} + 3\,S^{--} = 2\,\mathbf{CoS}\ \text{(black)} + \mathbf{S} + 12\,NH_3$$

7. Dissolving of CoS by aqua regia.

$$3\,CoS + 2\,NO_3^- + 8\,H^+ + 12\,Cl^- = 3\,CoCl_4^{--} + 2\,NO + 3\,\mathbf{S} + 4\,H_2O$$

8. Oxidation of $Co(OH)_2$ to $Co(OH)_3$.

$$2\,\mathbf{Co(OH)_2}\ \text{(blue)} + H_2O_2\ \text{(alkaline solution)} = 2\,\mathbf{Co(OH)_3}\ \text{(black)}$$

9. Reduction of Co(III) to Co(II) by chloride ion.

$$2\,\mathbf{Co(OH)_3} + 2\,Cl^- + 6\,H^+ = 2\,Co^{++} + Cl_2 + 6\,H_2O$$

10. Identification of cobalt(II) ion. The cobalt ion is treated with a saturated solution of NH_4SCN in ethyl alcohol.

$$Co^{++} + 4\,SCN^- \rightleftarrows Co(SCN)_4^{--}\ \text{(deep blue;}$$

unstable in water solution but stable in alcohol)

Nickel

33.17 Mine production, in tons (1950). World, 159,500; Canada, 122,800; U.S.S.R., 27,500; New Caledonia, 6900; U.S., 913; U.S. consumption, 98,900; U.S. imports, 91,553.

33.18 Occurrence. The most important nickel ores are pentlandite, $NiS \cdot 2FeS$; and garnierite, $(Ni,Mg)SiO_3$. They are generally associated with iron, copper, and cobalt ores.

33.19 Metallurgy. The preparation of pure nickel from its ores is a complicated process, because it is always found associated with other metals, particularly cobalt, iron, and copper.

33.20 Properties (see Table 33.1). It is hard, very malleable, and takes a very high polish.

33.21 Uses. Nickel is used for the manufacture of alloy steel (40%), nonferrous alloys (34%), nickel anodes and salts for nickel plating (18%), cast iron (4.8%), and nickel compounds (3.2%). Finely divided nickel, prepared from nickel compounds, is used as a catalyst in many organic chemical reactions, notably hydrogenation of vegetable oils to produce fat substitutes. Some nickel is used in making nickel coins (25% Ni, 75% Cu).

33.22 Important commercial compounds and their uses

1. $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$. Electrolyte in nickel-plating baths.
2. $Ni(CO)_4$, nickel carbonyl. It is a unique compound (a colorless liquid which boils at 43.2°C) which is formed when CO gas is passed over nickel at 30–50°C. At temperatures above 100°C the vapor decomposes into Ni and CO. Since none of the other metals that occur with nickel forms a stable carbonyl in the 30–120°C temperature range, its formation and subsequent decomposition provide a means of preparing pure nickel from its ores (the Mond process).
3. NiO_2. Manufacture of Edison cells (see 25.1).

33.23 Reactions. Its principal oxidation state is +2, with an unstable state of +4. In contrast to iron and cobalt, it has no +3 state.

1. $Ni = Ni^{++} + 2e$; $E^\circ = 0.25$ volt.
2. The metal reacts slowly with dilute nonoxidizing acids.

$$Ni + 2\,H^+ = Ni^{++} + H_2$$

3. Nickel dissolves rapidly in nitric acid and aqua regia.

$$3\,Ni + 2\,NO_3^- + 8\,H^+ = 3\,Ni^{++} + 2\,NO + 4\,H_2O$$

$$3\,Ni + 2\,NO_3^- + 8\,H^+ + 12\,Cl^- = 3\,NiCl_4^{--} + 2\,NO + 4\,H_2O$$

4. Precipitation of $Ni(OH)_2$ in the separation and identification of nickel

$$Ni^{++} + 2\,OH^- = \mathbf{Ni(OH)_2}\ \text{(green)}$$

5. Formation of the complex ammine ion. In keeping with its character as a transition metal, nickel forms colored salts and many complex ions.

$$\mathbf{Ni(OH)_2} + 6\,NH_3 = Ni(NH_3)_6^{++} + 2\,OH^-$$

6. Precipitation of NiS in analytical separation.

$$Ni(NH_3)_6^{++} + S^{--} = \mathbf{NiS}\ \text{(black)} + 6\,NH_3$$

7. Identification of Ni^{++}.

$Ni(NH_3)_6^{++} + 2\ (CH_3)_2C_2(NOH)_2$ (dimethyl glyoxime) = $\mathbf{NiC_8H_{14}N_4O_4}$ (strawberry red) + $2\ NH_4^+ + 4\ NH_3$

$$\mathbf{Ni(OH)_2} + BrO^- = \mathbf{NiO_2 \cdot H_2O}\ (\text{black}) + Br^-$$

Questions

1. Trace the process whereby hematite iron ore containing sand as impurity is converted to pig iron in the blast furnace.

2. What is steel? How can pig iron be converted into steel?

3. Upon what factors do the properties of steel depend?

4. Point out what happens when pure iron rusts in the air.

5. Why does contact with copper cause iron to rust faster?

6. Enumerate the methods that are used to keep iron from rusting.

7. Show by equations how Fe^{++}, Fe^{+++}, Co^{++}, and Ni^{++} can be identified.

8. Point out the characteristics of iron, cobalt, and nickel which identify them as transition elements.

9. Why are transition metals generally used in the preparation of alloy steels?

10. Write equations to show the oxidation of Fe(II), Co(II), and Ni(II) to Fe(III), Co(III), and Ni(IV), respectively.

11. Point out briefly how the hardness of a piece of 1% carbon steel is altered when it is subjected to heat treatment.

12. What is case hardened steel, why is it useful, and how is it prepared?

13. For the blast furnace process give: (a) the raw materials used; (b) the general features of the construction of the furnace; (c) the reactions that take place in the furnace; (d) the products formed and the use of each.

14. Account for the fact that when a piece of soft iron wire is flattened a bit by pounding with a hammer, it breaks off easily at the flattened spot.

15. Point out what takes place when a blueprint of a black line tracing is prepared.

16. Account for the fact that a blue-black ink is first blue, then changes to a permanent black.

17. Show, by balanced equations, oxidation by Fe(III) in acid solution and in alkaline solution.

18. Account for the fact that Fe^{+++} will oxidize I^- but not Br^-.

19. How is cobalt-60 prepared and for what is it used?

20. Give the reactions that take place when the Edison cell discharges and also when it is recharged.

CHAPTER 34

The Alkaline Earth Metals

34.1 The elements of group IIA. Some properties of the group IIA elements are given in Table 34.1. An examination of this table and a study of the behavior of each of the IIA elements and their compounds will bring out the following facts and relationships.

TABLE 34.1

PROPERTIES OF GROUP IIA ELEMENTS

Element	Period	At. no.	At. wt	At. diam, Å	Ion diam, Å	Electron configuration	Oxid. no.	$E°$ $M = M^{++} + 2e$	Density	Mp °C	Bp °C
Beryllium	2	4	9.013	1.78	0.34	2, 2	2	1.85	1.86	1350	1500
Magnesium	3	12	24.32	2.73	0.78	2, 8, 2	2	2.37	1.75	651	1110
Calcium	4	20	40.08	3.47	1.06	2, 8, 8, 2	2	2.87	1.55	810	1170
Strontium	5	38	87.63	3.83	1.27	2, 8, 18, 8, 2	2	2.89	2.60	800	1150
Barium	6	56	137.36	3.96	1.43	2, 8, 18, 18, 8, 2	2	2.90	3.61	850	1140
Radium	7	88	226.05	4.56	1.52	2, 8, 18, 32, 18, 8, 2	2	2.92	5.0	960	1140

1. Each element in the group has only 2 electrons in its valence shell. There are no incomplete inner subshells.

2. Each element exists in its compounds in only one oxidation state, +2. This state is represented by the dipositive cation, M^{++}. This single oxidation state of +2 is in line with the concept that the valence shell contains only 2 electrons, and there are no incomplete inner subshells. Because of this single oxidation state, the only oxidation-reduction reactions encountered in the study of these metals are those in which the ion changes to the metal or the metal changes to the ion.

3. The elements all have relatively large atomic diameters, the distance from the valence electrons to the nucleus being thus comparatively large. These electrons are not firmly bound and are easily re-

moved. As a result, the elements are strongly electropositive. This is indicated by their high reactivity and high positive oxidation potentials.

4. The elements are all characteristically metallic in that they are good conductors, are highly ductile and malleable, and acquire a bright luster when polished.

5. The oxides and hydroxides are all basic. This is in line with the large size of the ions and the consequent high electropositivity of the elements.

6. The compounds (salts, oxides, hydroxides, hydrides) are all electrovalent. This is in line with the high electropositivity of the elements.

7. The elements form colorless cations. This is in line with the fact that there are no incomplete inner subshells.

8. The elements show slight tendency to form complex ions. This is in line with the fact that there are no incomplete inner subshells and the ions are comparatively large.

9. As the atomic number increases, the following changes in properties of the elements and their compounds are noted.

(a) The electropositivity, as represented by the oxidation potential, increases.

(b) The strength of the element as a reducing agent increases. This is in line with the increase in oxidation potential.

(c) The atomic diameter increases.

(d) The ionic diameter increases.

(e) The hydroxide becomes more basic in character: $Be(OH)_2$ is the least basic and is actually amphoteric in character; $Ra(OH)_2$ is the most strongly basic. This is in line with the increase in size of the ion.

(f) The solubility of the hydroxide in water increases: $Be(OH)_2$ is only very slightly soluble, $Mg(OH)_2$ is slightly soluble, while the others are moderately soluble to an increasing degree.

(g) The rate at which they react with dilute acids, with water, and with nonmetals increases. Beryllium is only slowly attacked by dilute acids, while barium reacts violently. Likewise, the rate of reaction of beryllium with water is practically negligible, while barium reacts rapidly. All six metals tarnish when exposed to air.

(h) The solubility in water of their sulfates decreases: $BeSO_4$ dissolves to the extent of about 300 g/l of solution, while less than 0.002 g of $RaSO_4$ will dissolve in a liter.

10. The four most reactive members of the group give characteristic colors to the flame (calcium, brick red; strontium, crimson; barium, green; radium, crimson). Beryllium and magnesium do not color the flame. The valence electrons of the elements of higher atomic number

and atomic diameter, being less firmly bound, are more easily dislodged. This thermal ionization, giving rise to flame spectra, is the cause of the coloration. Beryllium and magnesium, being less electropositive, are not so easily ionized, hence do not give visible spectra in the Bunsen flame.

11. The metal occurs in nature largely as the carbonate, sulfate, or silicate, never as the free metal (too reactive), the sulfide, or the oxide.

12. The free metal is prepared commercially by electrolysis of the melted chloride or hydroxide. The high reactivity of the metal makes reduction by carbon or other reducing agents impossible or impractical.

13. The two least reactive members of the group, beryllium and magnesium, are important because of the uses to which the metal itself is put. The other four members owe their importance largely to the uses of their compounds. Only magnesium, calcium, and radium will be discussed in detail.

Magnesium

34.2 Mine production, in tons (1950): World, 44,000; U.S., 15,726; United Kingdom, 5390; Canada, 1770. U.S. consumption, 19,784. 1952 U.S. production, 105,286. The tremendous upsurge in U.S. production from 1950 to 1952 is the result of the use of magnesium alloys in our accelerated defense program.

34.3 Occurrence. The most abundant magnesium minerals are: magnesite, $MgCO_3$; dolomite, $MgCO_3 \cdot CaCO_3$; brucite, $Mg(OH)_2$; 0.13% of sea water is Mg^{++}.

34.4 Metallurgy. All the magnesium produced in the United States in 1950 was obtained by electrolysis of fused $MgCl_2$, which was recovered from sea water. The following steps are involved in the metallurgical process (see Figure 34.1):

1. Sea water is pumped into huge tanks, where it is treated with a slurry of $Ca(OH)_2$. The $Ca(OH)_2$ is prepared from oyster shells ($CaCO_3$) by first heating to yield CaO:

$$CaCO_3 = CaO + CO_2$$

and then mixing with water to yield $Ca(OH)_2$:

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

The OH^- ions from the calcium hydroxide slurry react with the Mg^{++} ions in the sea water to give a precipitate of $Mg(OH)_2$.

$$Mg^{++} + 2\,OH^- = \mathbf{Mg(OH)_2}$$

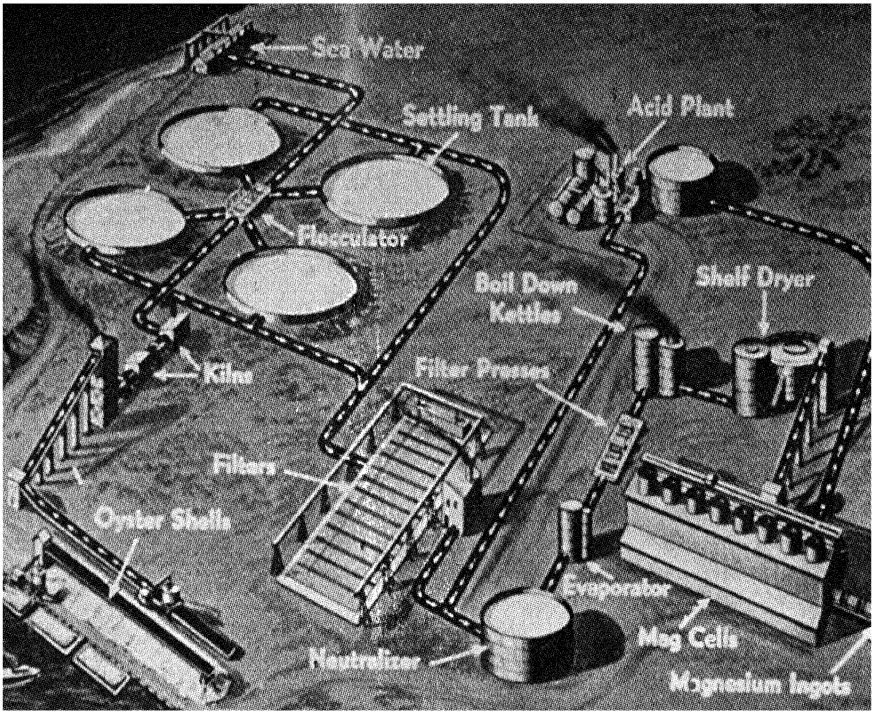


Figure 34.1. Steps in the production of magnesium from sea water. *(Courtesy Dow Chemical Company)*

2. The suspension of $Mg(OH)_2$ is concentrated by settling and is then run through large suction filters. The solid moist $Mg(OH)_2$ is digested with hot concentrated HCl, in which it dissolves to yield a solution of $MgCl_2$.

$$Mg(OH)_2 + 2\,H^+ + 2\,Cl^- = Mg^{++} + 2\,Cl^- + 2\,H_2O$$

This solution is evaporated to dryness to yield dry $MgCl_2$.

3. The $MgCl_2$ is melted and electrolyzed at temperatures above the melting point of magnesium (651°C) and the pure molten metal is drawn off and cast into billets (see Figure 34.2).

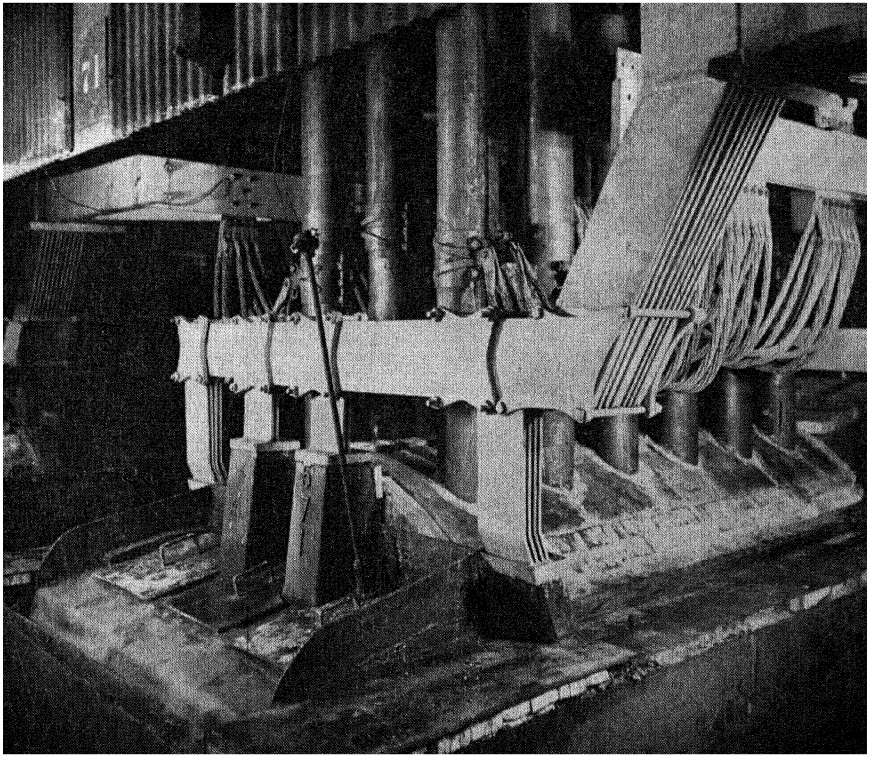
$$MgCl_2 = Mg + Cl_2$$

During the national emergency of 1940–1945, the anhydrous $MgCl_2$ for use in the electrolytic process was obtained from dolomite ($MgCO_3 \cdot CaCO_3$), brucite [$Mg(OH)_2$], and carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$) as well as from sea water. Also during this emergency, considerable amounts of magnesium were made by high-temperature reduction of magnesium oxide by carbon and by ferrosilicon. The electrolytic process is the most economical and is the only one in use at the present time.

34.5 Properties (see Table 34.1). A combination of lightness (density of 1.74), an attractive silver-white color, high ductility, malleability, and tensile strength, and ability to form useful alloys with many other metals makes magnesium a very desirable structural metal. Its outstanding fault is its high chemical reactivity, which makes it very susceptible to corrosion by acids and by the atmosphere.

34.6 Uses. Its chief use is in the manufacture of lightweight alloys for use in aircraft and all kinds of machines and appliances where a combination of light weight and moderately high strength is desired. The chief metals with which it is alloyed are aluminum, zinc, copper, manganese, beryllium, and zirconium.

Figure 34.2. Electrolytic cell for the production of magnesium by the electrolysis of melted magnesium chloride. The cylindrical columns are the graphite anodes. The laminated metal strips at the front (left) of the cell are copper bus bars attached to the carbon-lined tank which is the negative electrode of the cell. The molten magnesium formed in the electrolysis process is ladeled from the compartment at the front of the cell through the openings under the three-handled covers and is cast into billets. (*Courtesy Dow Chemical Company*)



34.7 Important commercial compounds and their uses

1. MgO. It is used for the manufacture of refractory brick and cement for use in furnace linings (blast, open-hearth, electric, etc.). About 377,000 tons were consumed in the U.S. in 1950.

2. $Mg(OH)_2$, milk of magnesia. It is used as a medicine for neutralizing stomach and mouth acidity and as a laxative.

3. $MgSO_4 \cdot 7H_2O$, Epsom salts. It is used as a laxative and also has numerous industrial uses.

4. $CaMg_3(SiO_3)_4$, calcium magnesium silicate, asbestos. The naturally occurring mineral is shredded and fabricated into various forms which are used as fireproof materials, boiler and furnace coverings, automobile brake linings, insulating materials, etc. Meerschaum, used for making pipes, and soapstone, used for making table tops and laboratory and industrial sinks and tanks, are also magnesium silicates.

5. $Mg_3(C_3H_4OHC_3O_6)_2$, magnesium citrate. It is used as a laxative.

34.8 Reactions (see 34.4)

1. $Mg = Mg^{++} + 2e$; $E^\circ = 2.37$ volts. Magnesium is strongly electropositive, very reactive, and a powerful reducing agent.

2. Rapid reaction of magnesium with dilute acids

$$Mg + 2\,H^+ = Mg^{++} + H_2$$

3. Rapid reaction of magnesium with steam. This accounts for the fact that a magnesium fire cannot be extinguished with small amounts of water. It can be extinguished with sand, and if not too large, with very large amounts of water.

$$Mg + H_2O = MgO + H_2$$

4. Magnesium is readily oxidized by most nonmetals.

$$2\,Mg + O_2 = 2\,MgO + 143{,}840 \text{ cal/mole}$$
$$Mg + Cl_2 = MgCl_2 + 153{,}400 \text{ cal/mole}$$

5. Reaction of magnesium with nitrogen. This is of interest as a potential method for the fixation of atmospheric nitrogen.

$$3\,Mg + N_2 = Mg_3N_2$$
$$Mg_3N_2 + 3\,H_2O \text{ (steam)} = 3\,MgO + 2\,NH_3$$

6. Reduction of CO_2 by magnesium. This explains why a magnesium fire cannot be extinguished with CO_2.

$$Mg + CO_2 = MgO + CO$$

7. Commercial manufacture of MgO from magnesite and brucite

$$MgCO_3 \text{ (magnesite)} + \text{heat} = MgO + CO_2$$
$$Mg(OH)_2 \text{ (brucite)} + \text{heat} = MgO + H_2O$$

8. Identification of the magnesium ion

$$Mg^{++} + NH_4^+ + PO_4^{---} = \mathbf{MgNH_4PO_4} \text{ (white, crystalline)}$$

Calcium

34.9 Occurrence. It constitutes 3.65% of the earth's crust, where it occurs as: limestone, $CaCO_3$; marble, $CaCO_3$; calcite, $CaCO_3$; fluorspar, CaF_2; gypsum, $CaSO_4 \cdot 2H_2O$; dolomite, $MgCO_3 \cdot CaCO_3$; rock phosphate, $Ca_3(PO_4)_2$; numerous silicates.

34.10 Metallurgy. It is prepared by electrolysis of melted $CaCl_2$. Less than 20 tons of metal were produced in the U.S. in 1950. About 40 tons of the metal and 250 tons of Ca—Si alloy were imported in 1950.

34.11 Properties (see Table 34.1). It is very reactive, relatively soft, and of low density.

34.12 Uses. Its chief use is as a deoxidizer and degasifier in the manufacture of steel and other alloys; it reacts with the oxygen and nitrogen to form compounds which are eventually removed as slag. It is used also as a reducing agent in organic synthesis.

34.13 Important commercial compounds and their uses. Calcium is significant chiefly because of the importance of its compounds.

A. $CaCO_3$. It occurs in nature as limestone, marble, calcite, pearls, oyster shells, clamshells, coral, chalk, and marl. About 120,000,000 tons of limestone were consumed in chemical processes in the United States in 1950. The important uses and the tonnages consumed by each were:

1. Manufacture of Portland cement, 55,219,000 (see 23.8)
2. As a metallurgical flux, 35,970,000 (see 25.10)
3. Manufacture of lime, CaO, 12,637,000. Lime is prepared in a rotary type furnace in which limestone is fed in at one end and CaO is removed at the other (see Figure 23.3).

$$CaCO_3 \text{ (heated)} = CaO + CO_2$$

4. Manufacture of sodium carbonate and sodium hydroxide, 6,174,350. The reactions that occur in the manufacturing process are discussed in Section 35.5.

5. Manufacture of glass, 769,680 (see 23.8)
6. Manufacture of calcium carbide, 749,930

$$CaCO_3 \text{ (heated)} = CaO + CO_2$$

A mixture of CaO and coke is heated in an electric furnace. Calcium carbide, CaC_2, is formed according to the following reaction.

$$CaO + 3\,C = CaC_2 + CO$$

7. Manufacture of sugar, 717,620. The $CaCO_3$ neutralizes the acidic components and at the same time aids in clarification of the sugar-containing liquor.
8. Manufacture of precipitated $CaCO_3$ (whiting), 676,410

$$CaCO_3 \text{ (heated)} = CaO + CO_2$$
$$CaO + H_2O = Ca(OH)_2\ (Ca^{++} + 2\,OH^-)$$

Carbon dioxide obtained from thermal decomposition of $CaCO_3$ is passed into the solution of $Ca(OH)_2$.

$$Ca^{++} + 2\,OH^- + CO_2 = \mathbf{CaCO_3} + H_2O$$

9. Direct use as an agricultural fertilizer aid, 616,840. It neutralizes the excess soil acidity.
10. Direct use as a component of stock foods, 463,050. It provides an alkalizing component and a source of calcium.

B. CaO, *Lime, or Quicklime.* About 7,000,000 tons were consumed in the United States in 1950. The major uses and the tonnages consumed by each use were:

1. Preparation of mortar in the building industry, 1,249,000
2. As a flux in the refining of steel, 1,132,000
3. Manufacture of paper, 618,000. The CaO serves as a neutralizing agent and as a source of the acid sulfite, which aids in the conversion of wood to pulp.
4. As an alkaline reagent in water purification, 566,700. It removes the temporary hardness by neutralizing the HCO_3^- ions, thereby allowing the $CaCO_3$ to precipitate.

$$Ca^{++} + HCO_3^- + OH^- = \mathbf{CaCO_3} + H_2O$$

It also reacts with the aluminum salts that are added, causing $Al(OH)_3$ to be precipitated. This $Al(OH)_3$ adsorbs and sweeps out impurities.

5. Manufacture of calcium carbide, 481,000 (see 34.13A)
6. Preparation of agricultural fertilizers, 332,700
7. Manufacture of glass, 210,300 (see 23.8)

C. $CaSO_4 \cdot 2H_2O$, *Gypsum.* It occurs as natural gypsum. About

8,193,000 tons of the crude ore were mined in the United States in 1950, the main production coming from Michigan, New York, Texas, Iowa, California, and Nevada. About 3,200,000 tons were imported. About 14% of this mined and imported ore was used in the form of the dihydrate as a retarder in the preparation of concrete and as an agricultural fertilizer (so-called *land plaster*). About 86% was calcined (heated) and thereby converted into *plaster of Paris.*

$$2\,CaSO_4 \cdot 2H_2O \text{ (heated)} = (CaSO_4)_2 \cdot H_2O \text{ (plaster of Paris)} + 3\,H_2O$$

About 96% of this calcined product was used in the manufacture of plaster, wallboard, lath, sheating, tile, and other building material. The use of the calcined product depends upon the fact that it reacts readily and quickly with water to form the original dihydrate.

$$(CaSO_4)_2 \cdot H_2O + 3\,H_2O = 2\,CaSO_4 \cdot 2H_2O + \text{heat}$$

D. CaF_2, *Fluorspar.* It occurs as natural fluorspar. A total of 301,510 tons were mined in the United States in 1950, and 164,634 tons were imported. About 56.5% of this CaF_2 was used as a flux in the manufacture of steel, 29% was used in the manufacture of HF, and 13% in the manufacture of ceramic enamel and glass.

E. CaC_2, *Calcium Carbide* (see 34.13A). About 490,000 tons were produced in the United States in 1950, practically all of it being used for production of acetylene (see 22.12).

$$CaC_2 + H_2O = CaO + C_2H_2 \text{ (acetylene)}$$

F. $CaCl_2$, *Calcium Chloride.* About 225,000 tons were consumed in the United States in 1950. The major part of this was produced as a by-product in the Solvay process for the manufacture of Na_2CO_3 (see 35.5B). The major uses are in the preparation of concrete, where it serves as a setting agent, and in the anhydrous form, for settling dust and for reducing the humidity of the air. The latter use depends upon its highly deliquescent character.

G. $Ca(ClO)_2$, *Calcium Hypochlorite, Bleaching Powder.* It is prepared by the reaction of chlorine with CaO in the presence of moisture.

$$2\,CaO + 2\,Cl_2 = CaCl_2 + Ca(ClO)_2$$

It is used as a disinfectant and bleaching agent.

$$CaCl_2 + Ca(ClO)_2 + 4\,H^+ = 2\,Ca^{++} + 2\,H_2O + 2\,Cl_2$$

H. $Ca_3(PO_4)_2$, *Calcium Phosphate, Rock Phosphate* (see 19.6).

34.14 Reactions (see 34.13)

1. $Ca = Ca^{++} + 2e$; $E^\circ = 2.87$ volts. Calcium is very reactive, strongly electropositive, and a powerful reducing agent.

2. Calcium reacts rapidly with cold water.

$$Ca + 2\,H_2O = Ca^{++} + 2\,OH^- + H_2$$

3. Calcium reacts rapidly with dilute acid.

$$Ca + 2\,H^+ = Ca^{++} + H_2$$

4. Calcium combines directly with hydrogen to form a stable hydride.

$$Ca + H_2 \text{ (heated)} = CaH_2$$

5. Calcium combines directly with nitrogen to form a stable nitride.

$$3\,Ca + N_2 = Ca_3N_2$$

6. Calcium burns rapidly in air.

$$2\,Ca + O_2 = 2\,CaO + 151{,}700 \text{ cal/mole}$$

7. Lime is strongly basic.

$$CaO + H_2O = Ca^{++} + 2\,OH^-$$

8. Identification of calcium ions

$$Ca^{++} + CO_3^{--} = \mathbf{CaCO_3} \text{ (white)}$$
$$Ca^{++} + C_2O_4^{--} = \mathbf{CaC_2O_4} \text{ (white)}$$

9. Erosion of limestone rocks by CO_2-laden water (see 21.16)

$$CaCO_3 + CO_2 + H_2O = Ca^{++} + 2\,HCO_3^-$$

The presence of Ca^{++} and HCO_3^- ions is the major cause of temporary hardness in water (see 13.15). This hardness can be removed by boiling or chemical treatment.

$$Ca^{++} + 2\,HCO_3^- + \text{heat} = \mathbf{CaCO_3} + H_2O + CO_2$$
$$Ca^{++} + 2\,HCO_3^- + 2\,OH^- = \mathbf{CaCO_3} + 2\,H_2O + CO_3^{--}$$

10. Reaction of CaH_2 with water. This is used by the armed forces and the weather bureau as a source of H_2 for filling observation balloons. It is also the basis for the use of CaH_2 as a reducing agent.

$$CaH_2 + 2\,H_2O = Ca^{++} + 2\,OH^- + 2\,H_2$$

11. Reaction of CaC_2 with nitrogen at high temperatures to yield calcium cyanamide. This was at one time an important nitrogen-fixation reaction (see 18.6).

$$CaC_2 + N_2 = CaCN_2 + C$$
$$CaCN_2 + 3\,H_2O \text{ (heated)} = CaCO_3 + 2\,NH_3$$

Radium

34.15 Occurrence. Radium is found, always and only, in uranium ores such as pitchblende, U_3O_8, and carnotite, $K_2O \cdot 2UO_3 \cdot U_2O_5 \cdot 3H_2O$. The reason is that radium is a product of radioactive disintegration of uranium as discussed in Section 8.6. The chief world deposits are in the Great Bear Lake area in Canada and the Belgian Congo in Africa. The most important United States deposits, consisting almost entirely of low-grade carnotite ores, are in the Colorado-Utah-Arizona area. Approximately 5000 mg of radium salts were produced from our domestic ores in 1950, with about 81,000 mg being imported. The average 1950 price of radium was $15,300 per gram. The increased use of radioisotopes such as cobalt-60 (see 33.15) has resulted in a reduced demand, and accordingly a reduced price for radium.

34.16 Metallurgy. Extraction of radium from uranium ores involves an extended process of solution and precipitation in which the radium appears as the carbonate, sulfate, and bromide.

34.17 Uses. The major use of radium is in the form of its salts, particularly $RaBr_2$ and $RaSO_4$, as a source of radiation in the treatment of cancer. This use depends upon the therapeutic effect of the radiation which is given off during the disintegration process. It also serves as a source of radiation for various kinds of research, and small quantities of the salt are used in the manufacture of luminous objects such as watch dials. The latter use depends upon the fact that the radium emanations cause certain substances such as ZnS to fluoresce. Synthetic radioelements, produced in nuclear reactors, have largely replaced radium for this use. The radioactive radon gas which is formed as a product in the decay of radium

$$_{88}Ra^{226} = {}_{86}Rn^{222} + {}_{2}He^{4} \text{ (alpha particle)}$$

is very commonly used as the direct source of radiation in medical therapy, the radium serving only as a source of the radon.

Questions

1. How do the following properties of the elements of Group IIA change with increase in atomic number? Account for these changes. (a) Atomic diameter; (b) ionic diameter; (c) oxidation potential; (d) reactivity; (e) basicity of the hydroxide; (f) density of the metal; (g) oxidation number.

2. Why do the metals of Group IIA form electrovalent compounds with electronegative elements?

3. Why do the ions of Group IIA show only a slight tendency toward hydration or complex ion formation?

4. Why are the group IIA ions colorless?

5. List the important uses of magnesium and indicate the properties that are the bases for these uses.

6. Why is calcium metal of relatively small industrial use?

7. List the important commercial calcium and magnesium compounds and point out the uses of each.

8. How are each of the following prepared? (a) Quicklime; (b) Portland cement; (c) plaster of Paris; (d) window glass; (e) superphosphate; (f) phosphorus; (g) magnesium; (h) calcium; (i) magnesium nitride; (j) calcium carbide.

9. How would you identify each of the following ions? Ca^{++}, Mg^{++}.

10. Account for the fact that the hydroxides of the metals of group IIA are strongly basic in character.

CHAPTER 35

The Alkali Metals

35.1 The elements of group IA. Some properties of the elements of group IA are summarized in Table 35.1. An inspection of this table and a detailed study of the chemical behavior of the individual elements bring out the following relationships and facts:

1. The group IA elements are all very reactive and very strongly electropositive metals. They have high oxidation potentials and are accordingly powerful reducing agents. Their atomic diameters are large; their oxides and hydroxides are accordingly strongly basic. This is all in line with the conclusion, already stated in Chapters 7 and 25, that as you proceed to the left in the periodic table, the elements become more strongly electropositive, the diameters of the atoms increase, and the oxides and hydroxides become more strongly basic. Cesium is one of the most reactive and most strongly electropositive of all metals and its hydroxide is the strongest base.

2. Each element has only 1 electron in its valence shell; there are no incomplete inner subshells. The combination of a single valence electron and a relatively large atomic diameter causes this electron to be given off readily to form a monopositive ion. This accounts for the

TABLE 35.1

PROPERTIES OF GROUP IA ELEMENTS

Element	Period	At. no.	At. wt	At. diam, Å	Electron configuration	Ionic diam, Å	$E°$, volts	Density	Mp °C	Bp °C	Flame color
Lithium	2	3	6.94	2.45	2, 1	1.20	3.045	0.53	179	1372	red
Sodium	3	11	22.997	3.17	2, 8, 1	1.90	2.714	0.97	97.9	880	yellow
Potassium	4	19	39.096	4.05	2, 8, 8, 1	2.66	2.925	0.86	62.7	776	violet
Rubidium	5	37	85.48	4.32	2, 8, 18, 8, 1	2.96	2.925	1.53	39.0	679	red
Cesium	6	55	132.91	4.70	2, 8, 18, 18, 8, 1	3.38	2.923	1.40	28.4	680	blue
Francium	7	87	(223)		2, 8, 18, 32, 18, 8, 1						

high reactivity and strongly electropositive character. Each element in the group exists in its compound in only one oxidation state, +1, represented by the monopositive cation M^+. Because of this single oxidation state the only oxidation-reduction reactions in which the elements take part are those in which the free element changes to an ion or vice versa.

3. The elements are all characteristically metallic in that they are excellent conductors of electricity and heat, acquire a mirrorlike luster when protected from oxidation (tarnishing), and are ductile and malleable. They are the softest and least dense of the solid metals. They are all silvery-white and waxlike. Their soft waxlike character and low densities are probably due to their large atomic diameters.

4. Because of their great reactivity they tarnish (oxidize) quickly when exposed to air.

5. They all react rapidly with cold water to liberate hydrogen and form a solution of the hydroxide. They combine directly with hydrogen and all nonmetals to form stable salts.

6. Their salts are, with a few exceptions, all soluble in water.

7. Their ions are all colorless and with only a few exceptions are simple (not complex). This tendency to form simple, colorless ions is in line with the postulate that their structures contain no incomplete inner subshells.

8. They all give characteristic visible colorations to the flame. This property is probably associated with the ease with which the electrons in the atom are displaced. The yellow of sodium and the violet of potassium serve as means of identification of these elements in qualitative analysis.

9. They show a closer similarity to each other than do the elements in any other group. This can be attributed to the ease with which the valence electron can be removed in each case, and emphasizes the role which the valence electrons play in determining the chemical behavior of an element.

10. The free element is, in most instances, prepared by electrolysis of the melted chloride or hydroxide. The choice of this method of preparation is made necessary by the high reactivity of the metal.

11. Because their compounds are as a rule soluble in water, they are found in solution underground, in the ocean, and in lakes; they also occur in the solid state in dried-up lake or ocean beds and in underground deposits that have through the past ages been out of contact with ground water.

12. Sodium and potassium are present in the earth's crust to the extent of 2.75% and 2.58%, respectively, and in ocean water to the

extent of 1.14% and 0.04%, respectively. The other group IA elements occur in nature in only trace amounts.

Sodium

35.2 Occurrence. Rock salt, NaCl, in underground salt mines; NaCl in sea water, certain inland lakes, and salt brine wells; Chile saltpeter, $NaNO_3$; borax, $Na_2B_4O_7$; Na_2CO_3 and Na_2SO_4 in certain lakes; complex silicates such as $NaAlSi_3O_8$.

35.3 Metallurgy. Sodium is prepared by electrolysis of melted NaCl. About 70,000 tons were manufactured in the United States in 1950.

35.4 Uses. About 64% of the total consumption of metallic sodium is used in the manufacture of tetra-ethyl lead, 11% in the manufacture of sodium cyanide, 11% in the manufacture of sodium alkyl sulfate, and 5% in the preparation of sodium peroxide.

35.5 Important commercial compounds and their uses. Sodium owes its great importance to the extensive use of its compounds. The number of these compounds is so large that it is beyond the scope of a book of this size to discuss all of them. Accordingly only a few of the most important will be considered.

A. NaCl, *Sodium Chloride, Common Salt.* As already noted, it occurs in nature in underground deposits of solid rock salt, in underground salt water, in ocean water, and in the water of certain inland lakes. It is obtained in the United States from the first two of these sources by ordinary bulk mining and by evaporation and crystallization. A total of 16,629,809 tons of NaCl was produced in the United States in 1950. About 43% of this total was solid salt, and 57% was in the form of a brine solution. About half of the solid salt was mined as rock salt and half was prepared by evaporation of brine solutions. The chief salt-producing states, in order of production, are Michigan, New York, Ohio, Louisiana, and Texas. The chief uses of salt and the approximate 1950 United States tonnages for each use are:

1. Manufacture of sodium carbonate, 6,379,000. The details of the manufacturing process will be discussed under sodium carbonate.

2. Manufacture of chlorine, sodium hydroxide, sodium hypochlorite, and sodium chlorate, 3,889,000.

When a water solution of NaCl is electrolyzed in a cell (see Figure 35.1) which does not allow the products to mix, Cl_2, H_2, and NaOH are

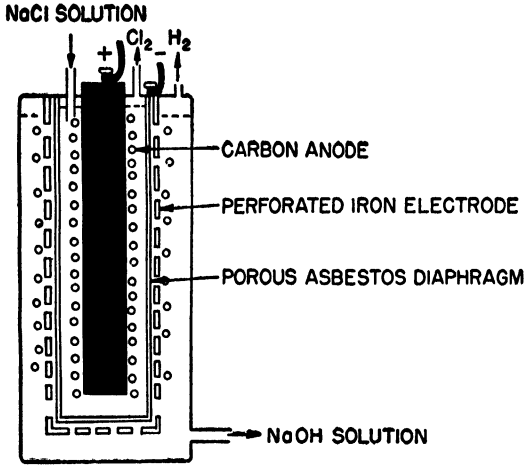


Figure 35.1. Nelson-type cell for the commercial preparation of NaOH, Cl_2 and H_2 by electrolysis of brine solution.

formed according to the reaction represented by the molecular equation

$$2\ NaCl + 2\ H_2O = Cl_2 + 2\ NaOH + H_2$$

If the chlorine that is liberated is allowed to react at room temperature with the NaOH that is formed, NaClO (sodium hypochlorite) will be produced according to the reaction

$$Cl_2 + 2\ NaOH = NaCl + NaClO + H_2O$$

If the reaction takes place at higher temperatures, $NaClO_3$ is formed according to the molecular equation

$$3\ NaClO\ (heated) = 2\ NaCl + NaClO_3$$

3. Packing, curing, and seasoning of meat, fish, dairy products, and other foods, 1,861,000.

4. Consumption by farm livestock and other farm uses, 956,000.

5. Manufacture of other chemicals, 914,000. The use of NaCl for the manufacture of HCl has already been discussed (see 16.6).

6. Ice and dust control on highways and railroads, 566,000.

7. Water softener regeneration, 548,000 (see 13.15).

8. Brine for refrigeration systems, 182,000.

9. Manufacture of sodium, 93,000.

B. Na_2CO_3, *Sodium Carbonate.* It occurs in the natural salt deposits from dried-up lakes such as Searles Lake and Owens Lake in California and Great River in Wyoming. About 351,000 tons of Na_2CO_3 were removed from these natural deposits in the United States in 1950, while

about 4,000,000 tons were manufactured by the *Solvay process* (see Figure 35.2). In this process a mixture of CO_2 and NH_3 gases is passed into a solution of NaCl of definite concentration at a definite temperature. Sodium bicarbonate is formed as a result of the reaction represented by the molecular equation

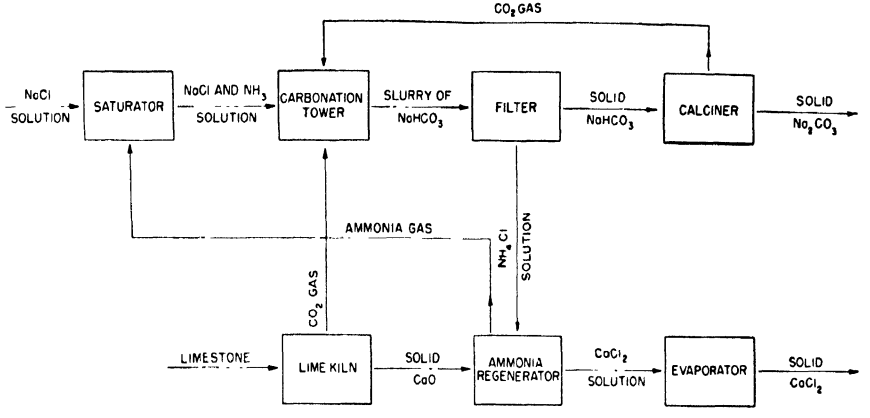


Figure 35.2. Schematic representation of the Solvay process for the manufacture of sodium carbonate from limestone and common salt.

$$CO_2 + NH_3 + NaCl + H_2O = NaHCO_3 + NH_4Cl$$

The $NaHCO_3$, being the least soluble of the products, crystallizes out. It is converted to Na_2CO_3 by heating.

$$2\,NaHCO_3\ (\text{heated}) = Na_2CO_3 + H_2O + CO_2$$

The CO_2 liberated in this reaction is recyled to yield more $NaHCO_3$. The CO_2 consumed in the process is formed by thermal decomposition of limestone.

$$CaCO_3\ (\text{heated}) = CaO + CO_2$$

The CaO formed in this latter reaction is made to react with the NH_4Cl which remains in the solution from which $NaHCO_3$ has precipitated, thereby regenerating the NH_3 which is needed.

$$CaO + 2\,NH_4Cl = 2\,NH_3 + H_2O + CaCl_2$$

The $CaCl_2$ is used as described in Section 34.13F.

The important uses of Na_2CO_3 and the approximate tonnages consumed by each use in the United States in 1950 are:

1. Manufacture of glass, 1,225,000 (see 23.8).
2. Manufacture of soap, sodium hydroxide, and sodium bicarbonate,

805,000. Soap is obtained by the reaction of a solution of Na_2CO_3 with either the free stearic acid or the glyceryl stearate, palmitate, and oleate contained in tallow or cottonseed oil.

$$Na_2CO_3 + 2\ C_{17}H_{35}COOH \text{ (stearic acid)} = 2\ C_{17}H_{35}COONa \text{ (soap)} + H_2O + CO_2$$

$$2\ C_3H_5(C_{17}H_{35}COO)_3 \text{ (stearin)} + 3\ Na_2CO_3 + 3\ H_2O = 2\ C_3H_5(OH)_3 \text{ (glycerine)} + 6\ C_{17}H_{35}COONa + 3\ CO_2$$

The reactions are carried out at temperatures near 100°C.

In the so-called *lime-soda process* for the manufacture of NaOH, Na_2CO_3 and $Ca(OH)_2$ are brought together in solution and react according to the equation

$$Ca^{++} + 2\ OH^- + 2\ Na^+ + CO_3^{--} = \mathbf{CaCO_3} + 2\ Na^+ + 2\ OH^-$$

The $CaCO_3$ is filtered off and the NaOH is recovered by evaporation of the resulting solution nearly to dryness.

When CO_2 gas is passed into a cold, concentrated solution of Na_2CO_3, $NaHCO_3$ is precipitated according to the reaction

$$2\ Na^+ + CO_3^{--} + CO_2 + H_2O = 2\ \mathbf{NaHCO_3}$$

3. Manufacture of other chemicals, 1,050,000. In the majority of cases the Na_2CO_3 neutralizes the excess acid involved in the process.

4. Metallurgy of aluminum and some of the less familiar metals, 245,000.

5. Water-softening agents, 210,000. The Na_2CO_3 precipitates as carbonates the heavy metal ions that cause hardness (see 13.15).

6. Manufacture of pulp and paper, 200,000.

7. Manufacture of textiles, 65,000.

8. Refining of petroleum, 24,000.

C. $NaHCO_3$, *Sodium Hydrogen Carbonate, Sodium Bicarbonate.* Although the actual tonnage of this compound is not large, it is of practical interest to everyone because of its familiar use as *baking soda* and its presence in *baking powder.* The function of baking soda and baking powder in causing dough to rise depends upon liberation of CO_2 from $NaHCO_3$ either by heat or by the H^+ ions released by a component of the baking powder [$KHC_4H_4O_6$ in cream of tartar powders, $Ca(H_2PO_4)_2$ in phosphate powders, and $Na_2SO_4 \cdot Al_2(SO_4)_3$ in alum powders]. Large amounts of $NaHCO_3$ are now used in the preparation of a dry fire extinguisher which functions by virtue of the release of CO_2 when the solid $NaHCO_3$ is heated.

$$2\,NaHCO_3\ (\text{heated}) = Na_2CO_3 + H_2O + CO_2$$
$$HCO_3^- + H^+ = H_2O + CO_2$$

D. NaOH, *Sodium Hydroxide, Caustic Soda.* Of the approximately 3,000,000 tons of NaOH that were consumed in the United States in 1950, about 85% was produced by the electrolysis of brine solution (35.5A2) and 15% was produced by the lime-soda process (35.5B2). The most important uses of NaOH and the approximate 1950 tonnages are:

1. Manufacture of various organic and inorganic chemicals, 500,000. The NaOH functions as a base and neutralizes the excess acid used in the process, or it acts as a reactant in the formation of the compound.

2. Manufacture of rayon and cellophane, 460,000. Cellulose, derived from cotton or wood pulp, is converted to cellulose xanthate by treatment first with NaOH, then with CS_2. The xanthate is then dispersed in a dilute solution of NaOH. This dispersion, called *viscose*, is forced through a finely perforated nozzle into a dilute solution of sulfuric acid and sodium sulfate. The fine xanthate stream is immediately converted into a thin filament of cellulose, and these filaments are twisted into a thread of rayon. Cellophane is of the same composition as rayon and is made by the same process except that it is formed into sheets rather than filaments.

3. Refining of petroleum, 183,000. The NaOH functions largely as a base to neutralize the excess acid used in the process.

4. Manufacture of soap, 165,000. The NaOH neutralizes the free stearic and palmitic acids or saponifies the vegetable oils and tallow that are used as raw materials.

$$Na^+ + OH^- + C_{17}H_{35}COOH\ (\text{stearic acid}) = C_{17}H_{35}COONa\ (\text{soap}) + H_2O$$
$$3\,Na^+ + 3\,OH^- + C_3H_5(C_{17}H_{35}COO)_3 = 3\,C_{17}H_{35}COONa + C_3H_5(OH)_3\ (\text{glycerine})$$

5. Manufacture of various textiles, 130,000.

6. Manufacture of pulp and paper, 83,000.

E. $NaNO_3$, *Sodium Nitrate.* It occurs naturally as Chile saltpeter. Its major use is in the compounding of fertilizers. Small amounts are used in the manufacture of nitric acid by treatment of the dry salt with concentrated sulfuric acid.

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3$$

F. Na_2SO_4, *Sodium Sulfate.* It is used in the manufacture of paper, rayon, and glass.

G. *Other Less Important Sodium Compounds and Their Common Uses*

1. $Na_2B_4O_7$, sodium tetraborate, borax; soap powders.

2. $Na_2S_2O_3$, sodium thiosulfate, hypo; fixing agent in photography and antichlor in bleaching.

3. Na_3PO_4, trisodium phosphate; washing powders, cleansing agents, and paint removers.

4. Na_2SiO_3, sodium silicate, water glass; manufacture of paper and soap.

5. NaCN, sodium cyanide; extraction of silver and gold from their ores and the preparation of silver, gold, and copper electroplating solutions.

35.6 Reactions of sodium

1. $Na = Na^+ + e$; $E^\circ = 2.714$ volts. Sodium is very reactive and a powerful reducing agent.

2. Sodium reacts vigorously with cold water.

$$2\,Na + 2\,H_2O = H_2 + 2\,Na^+ + 2\,QH^-$$

3. Sodium reacts violently with dilute acids.

$$2\,Na + 2\,H^+ = 2\,Na^+ + H_2$$

4. Sodium combines with hydrogen, when heated, to form a stable hydride.

$$2\,Na + H_2 = 2\,NaH$$

The melted hydride is a conductor of electricity, and on electrolysis yields metallic sodium at the negative electrode (cathode) and hydrogen gas at the positive electrode (anode). This indicates that NaH is a salt in which the hydrogen exists as the negative hydride ion, H^-. Sodium hydride reacts with cold water to liberate hydrogen.

$$NaH + H_2O = Na^+ + OH^- + H_2$$

5. Sodium combines with all nonmetals to form binary salts.

$$2\,Na + Cl_2 = 2\,NaCl$$

6. Sodium salts are, as a general rule, soluble in water. The formation of the slightly soluble compound $NaZn(UO_2)_3(C_2H_3O_2)_9$ as a yellow, crystalline precipitate when sodium ions react with a solution of zinc uranyl acetate is a moderately sensitive identification test. The fluffy yellow coloration which is produced when sodium salts are heated in the open flame of the gas burner is a very sensitive test.

Potassium

35.7 Production of potassium salts. The importance of potassium attaches to the fact that it is necessary for the development of the seeds and fruits of most plants, and hence is an essential fertility component of all soils. Most soils are deficient in potassium; therefore it must generally be added as a fertilizer. Because the supply of naturally occurring potassium salts in the world is limited and because the agricultural demands for potassium are so great, practically all of it is used, in the form of KCl, K_2CO_3, and K_2SO_4, as fertilizer. The 1950 production figures for potassium salts calculated as tons of K_2O are: World, 4,840,000; U.S. 1,286,762; France, 1,118,000; Germany, 1,003,000; Spain, 167,000; New Mexico, 1,086,996; U.S. consumption, 1,409,000; U.S. imports, 199,493. The phenomenal increase in production of potash in the United States in the past 40 years is indicated by the fact that our 1915 production was only 4374 tons, while the 1952 production was about 1,580,000 tons.

35.8 Occurrence. The most important potassium minerals are: orthoclase feldspar, $KAlSi_3O_8$; carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$; langbeinite, $K_2SO_4 \cdot 2MgSO_4$; sylvite, KCl; polyhalite, $K_2SO_4 \cdot 2CaSO_4 \cdot MgSO_4 \cdot 2H_2O$; kainite, $MgSO_4 \cdot KCl \cdot 3H_2O$; schonite, $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$.

The most important ores found in the United States are the deeply buried sylvite and langbeinite deposits in the Carlsbad regions of southeastern New Mexico. The Stassfurt deposits in Germany and Alsace, containing carnallite, sylvite, schonite, polyhalite, and kainite are world famous, and prior to 1920 were the only large source of potash.

35.9 Metallurgy. Very little potassium is manufactured. It is prepared by the reaction of Na with K_2CO_3 at high temperatures.

$$2\,Na + K_2CO_3 = 2\,K\ (gas) + Na_2CO_3$$

The more volatile K (bp 776°C) can be distilled off. Electrolysis of melted KOH and KCl is unsatisfactory because potassium dissolves in the molten compound.

35.10 Important commercial compounds and their uses

1. KNO_3. It is used in the manufacture of black powder, and in lesser quantities, as a preservative for meat. Black powder is a mixture of charcoal, sulfur, and potassium nitrate. The KNO_3 functions as the oxidizing agent, while the C and S are the reducing agents. The reaction,

once it is started by a spark, proceeds very rapidly and with evolution of much heat and a large volume of gas, which is a mixture of CO, CO_2, N_2, and SO_2. The principal solid products formed in the reaction are K_2CO_3, K_2SO_4, and K_2S.

2. Numerous potassium salts are used as chemical reagents. Potassium salts are as a rule less hygroscopic than the corresponding sodium salts and are therefore less liable to cake up in storage.

35.11 Reactions of potassium and its salts

1. $K = K^+ + e$; $E^\circ = 2.922$ volts. Potassium is a powerful reducing agent and is very reactive.

2. Potassium combines directly with hydrogen and all non-metals.

$$2\,K + Cl_2 = 2\,KCl$$

3. Potassium reacts violently with cold water and with dilute acids.

$$2\,K + 2\,H_2O\ (\text{cold}) = 2\,K^+ + 2\,OH^- + H_2$$

4. Identification of K^+ ions. With very few exceptions potassium salts are soluble in water. Formation of a yellow precipitate of the insoluble salt $K_2NaCo(NO_2)_6$ in the following reaction is a fairly sensitive test for potassium ions. Potassium compounds give a distinctive violet flame coloration.

$$2\,K^+ + Na^+ + Co(NO_2)_6^{---} = \mathbf{K_2NaCo(NO_2)_6}$$

[dipotassium sodium hexanitritocobaltate(III)]

5. Weathering of feldspars.

$$2\,KAlSi_3O_8\ (\text{feldspar}) + 2\,H_2O + CO_2 = Al(OH)_4Si_2O_5\ (\text{clay}) + 4\,SiO_2 + K_2CO_3$$

This is a very important reaction since it makes the potassium in natural feldspars soluble and hence available for use of plants.

Questions

1. Account for the strong electropositivity and great reactivity of the metals of group IA.

2. Point out what changes in properties take place in group IA with increase in atomic number and account for these changes.

3. Account for the presence of NaCl in sea water.

4. Why do metallic Na and K have few industrial uses?

5. List the more important potassium and sodium compounds and point out the uses of each.

6. Show, by equations, how the following can be prepared commercially. (a) Na_2CO_3; (b) $NaHCO_3$; (c) NaOH.

7. Show how K_2CO_3 is formed by the weathering of a feldspar $KAlSi_3O_8$.

8. How can the presence of potassium and sodium in a solution be detected?

CHAPTER 36

Some Important Less Familiar Elements

36.1 The inert gases

A. *Helium.* He; group 0; at. no. 2; at. wt 4; colorless gas; bp −268.9°C.

It occurs as a component of certain natural gas deposits in Texas, Kansas, and New Mexico. The United States Bureau of Mines, which is the world's only commercial producer of helium, recovered 81,394,416 cubic feet of the gas from this natural gas source in 1952. Its low density (4 g/22.4 l) and inertness make it an ideal gas for inflating balloons and dirigibles; practically all of it is used for this purpose. A mixture of 20 volume per cent of oxygen and 80 volume per cent of helium is used in place of air in diving chambers; because helium is only slightly soluble in water, only a small amount dissolves in the blood stream when the diver descends to depths of high pressure. As a result, the amount of gas that must be allowed to escape from the blood when the diver returns to normal pressures is so small that the feeling of discomfort known as "bends" is largely avoided. The low boiling point of helium (−268.9°C) is the basis for its use, in research laboratories, for obtaining extremely low temperatures; the helium is first liquefied; the liquid is then allowed to boil, a temperature of −268.9°C being thereby attained if the system is well insulated.

It occurs in the atmosphere to the extent of about 1 volume in 200,000. The alpha particles which are given off in radioactive decay are positively charged helium ions; consequently some helium gas is found in all uranium ores.

The fact that an alpha particle causes fluorescence when it strikes a substance such as zinc sulfide, and that this alpha particle is changed to an atom of helium gas when it picks up 2 electrons from the surroundings, is the basis for one method of determining the Avogadro number (the number of atoms per gram-atom or the number of molecules per mole). The number of helium atoms formed in a given length of time when radium decays can be determined by counting the fluorescent flashes on a zinc sulfide screen. The helium gas formed can be collected and its volume measured. From the volume occupied by a specific num-

ber of atoms of helium one can then calculate the number of atoms that would be present in 22.4 l of gas at STP.

B. *Neon.* Ne; group O; at. no. 10; at wt 20.183; colorless gas; bp −246.3°C.

It occurs in air to the extent of about 1 volume in 65,000 and is obtained commercially from this source by a process of fractional distillation and selective adsorption. Because of the characteristic color of its spectrum, and its inertness, it is widely used in the manufacture of neon lights.

C. *Argon.* A; group O; at. no. 18; at. wt 39.944; colorless gas; bp −185.8°C.

It occurs in air to the extent of about 0.94 volume per cent and is obtained from this source by fractional distillation. Practically all the gas is used in the manufacture of argon-filled electric light bulbs, its chemical inertness being the basis for this use; the presence of a gas in the bulb reduces the rate of vaporization of the tungsten filament.

36.2 Beryllium. Be; group IIA; at. no. 4; at. wt 9.02; density 1.8 g/cc; mp 1350°C; steel-gray metal.

Beryllium is finding increased use in the manufacture of high-strength, corrosion-resistant, lightweight, heat-treatable copper and nickel alloys. A copper alloy containing about 2.25% beryllium has the unique property of showing no "fatigue" on continued flexing, and is accordingly used for the manufacture of springs. The pure metal and the oxide are of great potential importance as moderators in nuclear reactors. Less than 100 tons of the metal were produced in the United States in 1950.

36.3 Germanium. Ge; group IVA; at. no. 32; at. wt 72.60; density 5.36; mp 960°C; bp 2700°C; silvery-white metal.

Germanium has come into great prominence because of its use in the manufacture of transistors (triode devices which perform the job of the conventional vacuum tube in radio and television circuits). Previous to the advent of the transistor, germanium was used largely in the manufacture of diode rectifiers for high-frequency electric currents in radio and television circuits and other devices; about 5 million such devices were used in the United States in 1951. Less than 100 tons of the metal were produced in the United States in 1950.

36.4 Molybdenum. Mo; group VIB; at. no. 42; at. wt 95.95; mp 2625°C; density 10.2; silver-gray metal.

The major use of molybdenum is in the manufacture of high-

temperature-resistant steel alloys for use in such equipment as gas turbines, jet aircraft engines, turbosuperchargers, and other devices where prolonged high temperatures are encountered. The 1950 United States production of 14,300 tons of molybdenum, consisting of molybdenum metal and various compounds, represented about 90% of the world output for that year.

36.5 Platinum. Pt; group VIIIB; at. no. 78; at. wt 195.23; mp 1774°C; bp 4400°C; density 21.4; silvery-white, nonreactive noble metal.

Platinum is one of the most corrosion-resistant of all metals. This is the basis for its use, in the laboratory, in the form of wire, for making flame tests, and in the form of crucibles, for fusion and evaporation of corrosive reaction mixtures. About 41% of the 1950 United States production of 18,100 troy ounces of platinum was used in the manufacture of jewelry, 37% as a catalyst in chemical industry (manufacture of H_2SO_4, NH_3 etc.), 15% for manufacture of electric contacts, and about 5% by the dental and medical profession for making inlays, supports, and surgical bindings. The price of platinum is about $100 per ounce.

36.6 Tantalum. Ta; group VB; at. no. 73; at. wt 180.9; mp 2800°C; bp 4100°C; density 16.6; silver-gray metal, high tensile strength, extremely resistant to corrosion.

Because of its combination of extreme resistance to oxidation and all types of chemical corrosion at low temperatures, and its high ductility and easy formability, it has come into wide use in the medical profession in surgical sutures and other repair items. Increasing percentages of the available supply of tantalum are being used in preparation of special steels for use in the manufacture of jet engines. It should be noted that niobium (columbium), which falls in the same group as tantalum, is even more desirable than tantalum as a component of jet-engine steels. Both metals confer upon steel the property of permanent high strength and stability even under the conditions of high temperature and high strain which prevail in jet-engine operation.

Less than 50 tons of tantalum and niobium were produced in the United States in 1950.

36.7 Titanium. Ti; group IVB; at. no. 22; at. wt 47.9; mp 1800°C; bp > 3000°C; density 4.5; silver-gray, high tensile strength, resistant to corrosion.

Up until about 1948 the production of titanium metal was inconsequential, the importance of the element centering entirely on the wide use of TiO_2 as a white paint pigment. Recent researches have brought

to light the unique and valuable character of titanium as an alloying component in the manufacture of special steels, with the result that production of the metal in the United States increased from a total of about 75 tons in 1950 to about 1100 tons in 1952. A total of 230,826 tons of TiO_2, largely for use as a paint pigment, was produced in the United States in 1950.

36.8 Tungsten. W; group VIB; at. no. 74; at. wt 183.92; mp 3370°C; bp 5900°C; density 19.3; silver-gray; hard, brittle; very resistant to corrosion.

Tungsten owes its importance to the wide use of the metal in the manufacture of filaments for electric light bulbs and in the manufacture of alloy steels and tungsten carbide, WC_2. The carbide is extremely hard and is used in the manufacture of cutting tools used for machining alloy steels. Our domestic production of tungsten is entirely inadequate to supply the industrial demand, with the result that we import from other nations about 23% of their total production.

36.9 Uranium. U; one of the actinides; at. no. 92; at. wt 238.07; silvery-white solid metal similar to nickel in appearance.

Prior to 1939 uranium was relatively unimportant, its chief claim to fame being the fact that its ores were the source of radium. The discovery of the fissionability of U-235 in 1939, the development of the process of converting U-238 into fissionable plutonium, and the use of U-235 and plutonium in atom bombs and nuclear reactions (see 8.14) has skyrocketed uranium to a position as the most critical and most sought-after of all the elements.

Uranium occurs as a number of minerals, the most important of which are pitchblende, U_3O_8, and carnotite, $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$. The world's richest deposits of uranium ore are found in the Great Bear Lake district in Canada and in the Belgian Congo. Although the ores found in the United States are low grade, they are being worked so intensively that the United States now ranks second to the Belgian Congo in production of uranium, Canada being third. Our carnotite ores, found chiefly in the Colorado-Utah-New Mexico area, are our commercial source of vanadium; uranium is therefore a by-product in the metallurgy of vanadium.

The uranium content of pitchblende and carnotite consists of about 99.3% U-238 and 0.7% U-235. The fissionable U-235 can be separated from the nonfissionable U-238 by a number of different processes, each of which depends for its effectiveness on the slight difference of three mass units in the mass numbers of the two isotopes. In one of these

processes the mixture of the two isotopes is converted into the hexafluoride gases, $U^{238}F_6$ and $U^{235}F_6$. This gas mixture is then separated into its two components by diffusion through thousands of porous plates, the rates of diffusion of the two gases being inversely proportional to the square roots of their molecular weights. Since the molecular weights of the two fluorides are 349 and 352, it is obvious that the difference in their rates of diffusion will be extremely small. In spite of this small difference, separation can be made if enough diffusion plates are used. Uranium-235 metal is obtained from the UF_6 by a chemical reduction process.

As has already been noted, U-235 can be fissioned by neutron bombardment. This is the basis for its use as the reactive component of the first A bomb. The fact that neutrons are given off when U-235 fissions and that these neutrons can sustain a chain reaction is the basis for the use of U-235 as a fuel in nuclear reactors.

Uranium-238 is converted to uranium-239 by neutron capture, and this U-239 decays radioactively with emission of a beta particle to form neptunium.

$$_{92}U^{238} + {}_{0}n^{1} = {}_{92}U^{239}$$
$$_{92}U^{239} = {}_{93}Np^{239} + {}_{-1}e^{0}$$

The neptunium has a very short half-life and disintegrates to form plutonium.

$$_{93}Np^{239} = {}_{94}Pu^{239} + {}_{-1}e^{0}$$

This plutonium is just about as readily fissioned as U-235 and can accordingly be used in place of the latter in atom bombs and nuclear reactors.

A mixture of U-238 and either U-235 or plutonium is the "fuel" in atomic energy furnaces. The heat evolved is the result of both the fission reaction and the reaction in which U-238 is changed to plutonium.

It should be noted that U-233 is about as readily fissionable by neutrons as is U-235. It does not occur in nature. However, it can be prepared from naturally occurring thorium by neutron bombardment in a reaction analogous to that in which plutonium is formed from U-238.

$$_{90}Th^{232} + {}_{0}n^{1} = {}_{90}Th^{233}$$
$$_{90}Th^{233} = {}_{91}Pa^{233} + {}_{-1}e^{0}$$
$$_{91}Pa^{233} = {}_{92}U^{233} + {}_{-1}e^{0}$$

This series of reactions, and the fissionability of U-233, indicate why thorium falls in a class with uranium as a strategic element.

The half-lives of the fissionable elements U-235, U-233, and Pu-239

TABLE 36.1

THE TRANSURANIUM ELEMENTS

Element	*Atomic number*	*Discovery date*	*Discoverers*	*Synthesis reactions*
Neptunium (Np)	93	1940	McMillan and Abelson	$_{92}U^{238} + {}_0n^1 = {}_{92}U^{239}$ $_{92}U^{239} \xrightarrow[23\ \text{min}]{-1e^0} {}_{93}Np^{239}$
Plutonium (Pu)	94	1941	Seaborg, McMillan. Wahl, and Kennedy	$_{93}Np^{239} \xrightarrow[2.3\ \text{days}]{-1e^0} {}_{94}Pu^{239}$ $_{92}U^{238} + {}_1D^2 = {}_{93}Np^{238} + 2\ {}_0n^1$ $_{93}Np^{238} \xrightarrow[2.0\ \text{days}]{-1e^0} {}_{94}Pu^{238}$
Americium (Am)	95	1944	Seaborg, James, and Morgan	$_{92}U^{238} + {}_2He^4 = {}_{94}Pu^{241} + {}_0n^1$ $_{94}Pu^{241} \xrightarrow[24\ \text{min}]{-1e^0} {}_{95}Am^{241}$
Curium (Cu)	96	1944	Seaborg, James, and Ghiorso	$_{94}Pu^{239} + {}_2He^4 = {}_{96}Cu^{242} + {}_0n^1$
Berkelium (Bk)	97	1949	Seaborg, Thompson, and Ghiorso	$_{95}Am^{241} + {}_2He^4 = {}_{97}Bk^{243} + 2\ {}_0n^1$
Californium (Cf)	98	1950	Seaborg, Thompson, Street, and Ghiorso	$_{96}Cm^{242} + {}_2He^4 = {}_{98}Cf^{244} + 2\ {}_0n^1$
	99	1954	*	$_{92}U^{238} + {}_7N^{14} = {}_{99}?^{247} + 5\ {}_0n^1$
	100	1954	*	$_{94}Pu^{239} + 15\ {}_0n^1 = {}_{100}?^{254} + 6\ {}_{-1}e^0$

* Work leading to the preparation of elements 99 and 100 was carried out, simultaneously, by teams of scientists at the University of California, the Argonne National Laboratory, the Los Alamos Scientific Laboratory, and the Atomic Energy Commission's Idaho testing reactor. The decision as to who shall be credited with the discovery has not yet been made.

are, respectively, 8.8×10^8 years, 1.63×10^5 years, and 2.41×10^4 years, while the half-life of U-238 is 4.498×10^9 years.

Uranium forms the uranyl ion UO_2^{++} which yields salts of the type $UO_2(NO_3)_2$. The insoluble yellow compound $UO_3 \cdot XH_2O$, which is formed when NH_4OH is added to solution of a uranyl salt, provides a convenient means of separating and identifying the UO_2^{++} ion.

$$UO_2^{++} + 2\,OH^- + H_2O = \mathbf{UO_3 \cdot XH_2O}$$

36.10 Vanadium. V; group VB; at. no. 23; at. wt 50.95; mp 1710°C; bp 3000°C; density 6.0; silver-gray metal.

Vanadium owes its importance to the fact that it is used in the manufacture of tool steels and other special alloy steels, about 90% of the annual consumption of the metal being for this purpose. As already noted in 36.9, the chief ore is carnotite, $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$, fairly extensive deposits of which are found in the Colorado-Utah-New Mexico area. The process by which the metal is obtained from this ore is quite involved. The United States leads the world in the production of vanadium; figures on the amount produced are, however, not available.

36.11 Zirconium. Zr; group IVB; at. no. 40; at. wt 91.22; mp 1900°C; bp 2900°C; density 6.52; silver-gray metal.

Zirconium has suddenly become a widely discussed metal because of its ability to withstand the high-temperature, high-intensity neutron bombardment encountered in nuclear reactors. It thus becomes a desirable metal for use in the construction of all sorts of nuclear energy equipment.

Crystal-clear samples of the ore zircon, $ZrSiO_4$, are used as precious stones in jewelry, and resemble diamonds in hardness and brilliancy.

36.12 The transuranium elements (neptunium, plutonium, americium, curium, berkelium, californium, and elements 99 and 100). These elements, all members of the actinide series with atomic numbers higher than that of uranium, do not occur in nature, but must be synthesized from other elements. These syntheses have all been accomplished since 1939.

Table 36.1 gives the names of the scientists who discovered each of these elements, the discovery date, and the synthesis reactions.

The transuranium elements are all radioactive. Plutonium-239 is the only one of any commercial importance at the moment; as has already been stated, it is fissionable by neutrons and is therefore used in making atom bombs and as a fuel in nuclear reactors.

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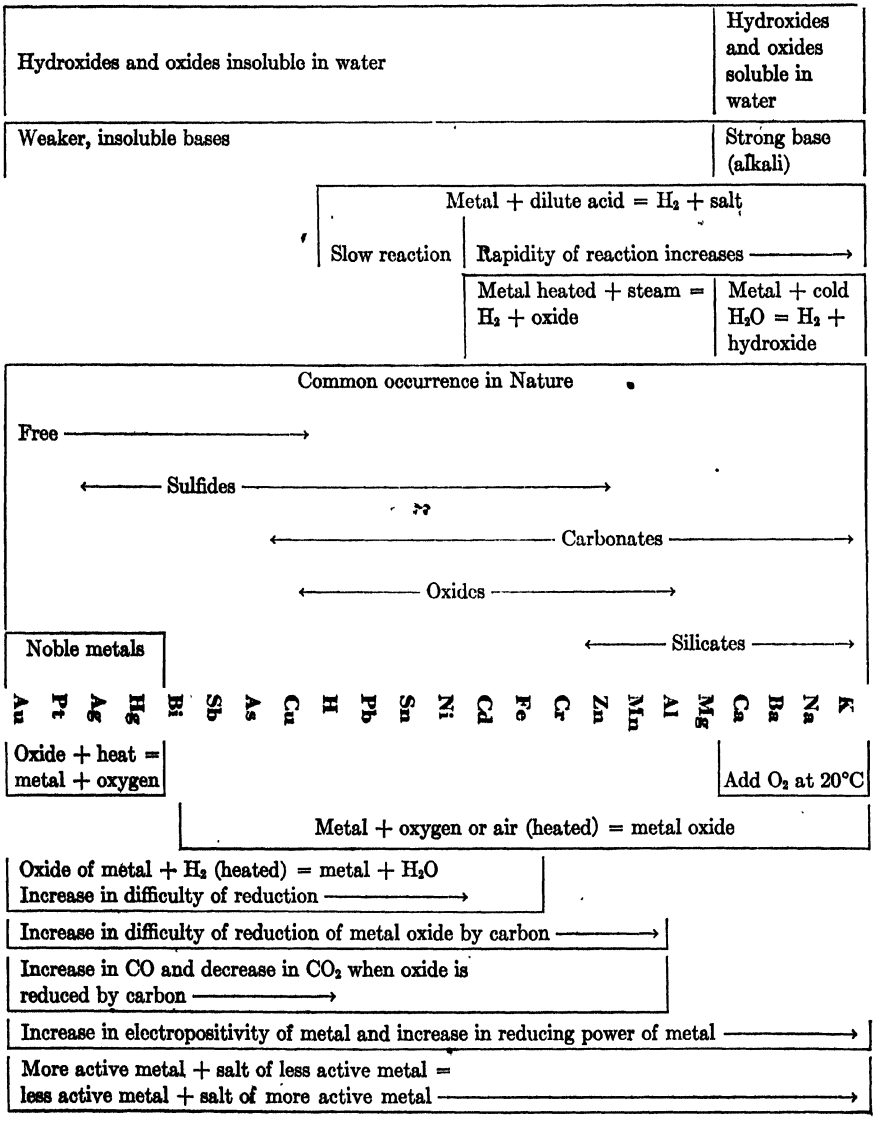
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THE ACTIVITY SERIES OF THE COMMON METALS



THE PERIODIC TABLE

Period	Orbitals	*s*		*d*										*p* (except He)					
	Character	Light metals		Heavy metals										Nonmetals					Inert gases
	Group	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
1	*	1.008 H 1																	4.003 He 2
2	*	6.940 Li 3	9.013 Be 4											10.82 B 5	12.01 C 6	14.01 N 7	16.00 O 8	19.00 F 9	20.18 Ne 10
3	*	23.00 Na 11	24.32 Mg 12											26.97 Al 13	28.06 Si 14	30.98 P 15	32.07 S 16	35.46 Cl 17	39.94 A 18
				Transition elements															
4	*	39.10 K 19	40.08 Ca 20	45.01 Sc 21	47.90 Ti 22	50.95 V 23	52.01 Cr 24	54.93 Mn 25	55.85 Fe 26	58.94 Co 27	58.69 Ni 28	63.54 Cu 29	65.38 Zn 30	69.72 Ga 31	72.60 Ge 32	74.91 As 33	78.96 Se 34	79.92 Br 35	83.7 Kr 36
5	*	85.48 Rb 37	87.63 Sr 38	88.92 Y 39	91.22 Zr 40	92.91 Nb 41	95.95 Mo 42	99 Tc 43	101.7 Ru 44	102.9 Rh 45	106.7 Pd 46	107.9 Ag 47	112.4 Cd 48	114.8 In 49	118.7 Sn 50	121.8 Sb 51	127.6 Te 52	126.9 I 53	131.3 Xe 54
6	*	132.9 Cs 55	137.4 Ba 56	138.9 La 57	178.6 Hf 72	180.9 Ta 73	183.9 W 74	186.3 Re 75	190.2 Os 76	193.1 Ir 77	195.2 Pt 78	197.2 Au 79	200.6 Hg 80	204.4 Tl 81	207.2 Pb 82	209.0 Bi 83	210 Po 84	211 At 85	222 Rn 86
7	*	223 Fr 87	226.1 Ra 88	227 Ac 89															

* Atomic weight
Symbol
Atomic number

	f orbitals													
Lanthanides Group IIIB	140.1 Ce 58	140.9 Pr 59	144.3 Nd 60	146 Pm 61	150.4 Sm 62	152.0 Eu 63	156.9 Gd 64	159.2 Tb 65	162.5 Dy 66	164.9 Ho 67	167.2 Er 68	169.4 Tm 69	173.0 Yb 70	175.0 Lu 71
Actinides	232.1 Th 90	231 Pa 91	238.1 U 92	239 Np 93	239 Pu 94	241 Am 95	242 Cm 96	243 Bk 97	244 Cf 98	247 99	254 100			