CHAPTER 1

FUNDAMENTALS OF CHEMISTRY

INTRODUCTION

Chemistry is the branch of science which studies matter—its composition, properties, and changes. Scientists attempt to discover and describe matter, then determine why these kinds of matter have particular characteristics and why changes in this matter occur. The discoveries of chemistry have greatly helped expand the life span of mankind, increase crop yields, and produce thousands of products that facilitate a higher standard of living. Most of today's medicines, plastics, synthetic fibers, alloys, pesticides, fertilizers, and many more products that enhance our lives are from the many discoveries of chemistry. Chemistry provides the foundation for the study and understanding of the biological sciences because without chemical reactions, life would not exist. Neither food nor clothing would be available. The energy needed for the human body to move and operate as well as all other biological processes would not exist without chemical reactions. Likewise, all processes involved in plant culture such as soil reactions, plant growth and development, pest management, and water use and quality, involve chemical reactions.

In developing a useful knowledge of chemistry, it is important to have a solid foundation and understanding of the fundamentals of chemistry. This foundation depends on a good understanding of the nature of elements and compounds and their relationships. The first three chapters of this book cover many of the concepts necessary to build this foundation required for turfgrass and agricultural managers and from which subsequent chapters are based and expanded upon.

Chemistry may be subdivided into several branches (Chart 1-1). These branches are not separate but overlap considerably.

Analytical chemistry deals with the separation, identification, and composition of all kinds of matter. Within analytical chemistry, *qualitative analysis* deals with the *separation* and *identification* of the individual components of materials while *quantitative analysis* determines *how much* of each component is present.
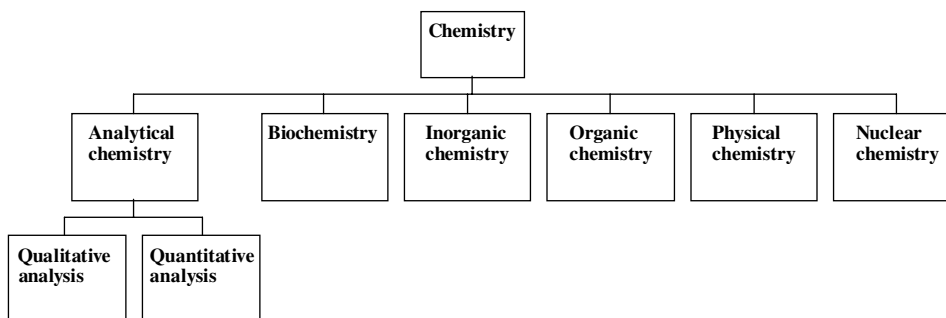
Chart 1-1. Branches of chemistry.

Biochemistry includes the study of materials and processes in living organisms.

Inorganic chemistry covers the chemistry of elements and their compounds except those containing carbon.

Organic chemistry is the study of carbon-containing materials.

Physical chemistry investigates the laws and theories of all branches of chemistry, especially the structure and transformation of matter and interrelationships of energy and matter.

Nuclear chemistry deals with the nuclei of atoms and their changes.

Turfgrass and agricultural science and management deals with all branches of chemistry with the possible exception of nuclear chemistry. This chapter introduces basic chemical concepts and topics necessary to use chemistry in agronomic practices covered in subsequent chapters.

ATOMS

The smallest particle of an element that has the properties of that element is an **atom** (from the Greek *atomos,* meaning ''indivisible''). **Molecules** are groups of two or more atoms held together by the forces of chemical bonds (Figure 1-1). Molecules are electrically neutral (no net charge). **Ions** are atoms or groups of atoms that carry positive or negative electrical charges.

An atom consists of two parts, the nucleus and the electron cloud. Every atom has a core, or **nucleus** (plural: nuclei) which contains one or more positively charged particles called **protons.** The number of protons distinguishes the atoms of different elements from one another. For example, an atom of hydrogen (H), the simplest element, has one proton in its nucleus; an atom of carbon (C) has six protons. For any element, the number of protons in the nucleus of its atoms is referred to its **atomic number.** The atomic number of hydrogen is one and the atomic number of carbon is six (Table 1-1).

Atomic nuclei also contain uncharged particles of about the same weight as protons called **neutrons.** Neutrons affect only the weight of the atom, not its chemical properties. The weight of an atom is essentially made up of the weight of the protons and neutrons in its nucleus. The **atomic weight** of an element is defined as the weight of an atom relative to the weight of a carbon atom having six protons
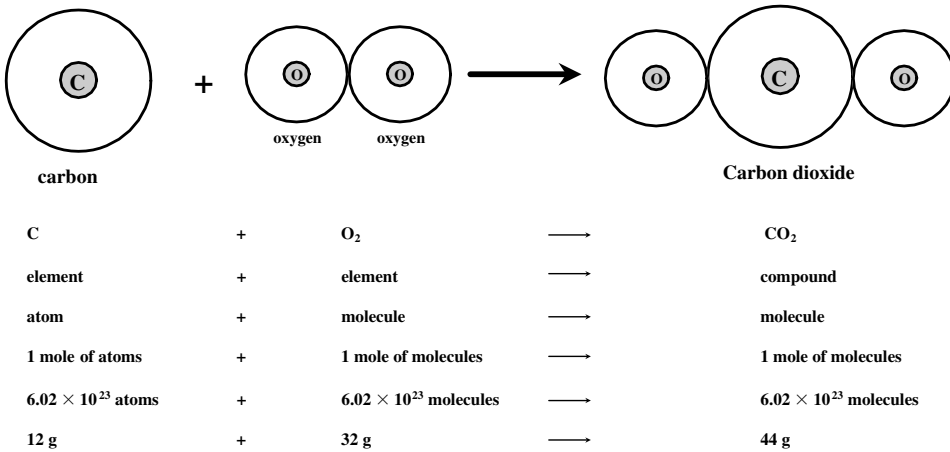
C	+	O_2	$\longrightarrow$	CO_2
element	+	element	$\longrightarrow$	compound
atom	+	molecule	$\longrightarrow$	molecule
1 mole of atoms	+	1 mole of molecules	$\longrightarrow$	1 mole of molecules
6.02×10^{23} atoms	+	6.02×10^{23} molecules	$\longrightarrow$	6.02×10^{23} molecules
12 g	+	32 g	$\longrightarrow$	44 g

Figure 1-1. Relationship between the number of atoms, molecules, moles, and grams when carbon (C) combines with oxygen (O_2) to form carbon dioxide (CO_2).

and six neutrons and a designated atomic weight of 12. Because these atomic weights are relative values, they are expressed without units of weight. Similarly, the **atomic mass** of an element is the mass of an atom relative to that of a carbon atom with a designated atomic mass of 12. The atomic structures of some elements are shown in Table 1-1.

atomic mass (proton + neutrons) − atomic number (or protons)

= number of neutrons in the nucleus

The remainder of an atom lies around the central nucleus and is called the electron cloud (Figure 1-2). The electron cloud gives an atom its volume and keeps other atoms out since two objects cannot occupy the same space simultaneously (often referred to as the *law of impenetrability*). Within the electron cloud, electrons revolve about the nucleus similar to the planets revolving about the sun, in orbits of various diameters dependent upon the available energy.

An electron cloud is composed of negatively charged particles, called **electrons** (Figure 1-2). Electrons are attracted by the positive charge of the protons. The number and arrangement of electrons determine whether an atom will react with itself or other atoms, and the manner in which the reaction will occur. Due to their opposite charges, protons attract electrons, and all atoms have an equal number of protons and electrons; thus all atoms are *electrically neutral*.

atomic number = number of protons = number of electrons

The Atomic Theory

An **atom** is the smallest unit of an element that can exist either alone or in combination with other atoms like it or different from it. In 1803, John Dalton attempted to explain why elements always combine in definite proportions and always con-

TABLE 1-1. Atomic Structures and Electronegativity of Some Essential Plant Elements

Element	Symbol	Common Oxidation (Valence) Numbers	Nucleus		Number of Electrons						Atomic Weight	Electro-negativity
			Atomic Number (Number of Protons)	Number of Neutrons	Total	1 (K)	2 (L)	3 (M)	4 (N)			
Essential Elements for Plants												
Hydrogen	H	+1	1	0	1	1	0	0	0	1	2.1
Boron	B	+3	5	6	5	2	3	0	0	11	2.0
Carbon	C	−4, +4	6	6	6	2	4	0	0	12	2.5
Nitrogen	N	−3, +5	7	7	7	2	5	0	0	14	3.0
Oxygen	O	−2	8	8	8	2	6	0	0	16	3.5
Magnesium	Mg	+2	12	12	12	2	8	2	0	24	1.5
Phosphorus	P	−3, +5	15	16	15	2	8	5	0	31	2.1
Sulfur	S	+6, −2	16	16	16	2	8	6	0	32	2.5
Potassium	K	+1	19	20	19	2	8	8	1	39	0.9
Calcium	Ca	+2	20	20	20	2	8	8	2	40	1.0
Manganese	Mn	+2, +3	25	30	25	2	8	8	7	55	1.5
Iron	Fe	+2, +3	26	30	26	2	8	8	8	56	1.8
Copper	Cu	+1, +2	29	35	29	2	8	8	11	64	1.9
Zinc	Zn	+2	30	35	30	2	8	8	12	65	1.6
Molybdenum	Mo	+3, +5	42	54	42	2	8	8	18[a]	96	1.8
Other Elements												
Sodium	Na	+1	11	12	11	2	8	1	0	23	1.0
Aluminum	Al	+3	13	14	13	2	8	3	0	27	1.5
Chlorine	Cl	−1	17	18	17	2	8	7	0	35	3.0

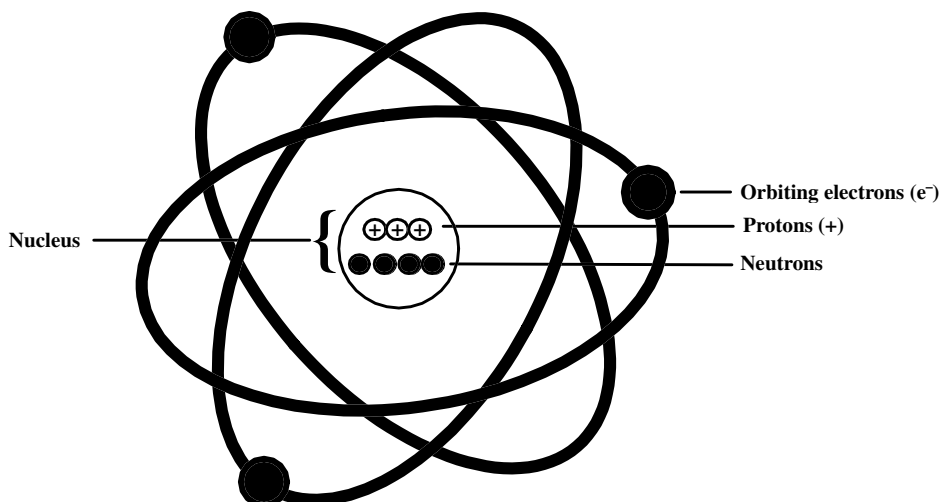[a]Molybdenum has 6 additional electrons in a 5th shell.

Figure 1-2. Atomic structure of lithium (Li). Atoms are made up of a relatively heavy, compact, centrally located nucleus which contains positively charged protons and neutrally charged neutrons. Lighter, negatively charged electrons orbit about the nucleus at varying distances from its center.

form to the Law of Conservation of Matter. Basically, for each element there is a chemical or reactive unit, called an *atom,* which has its own characteristic weight. In chemical reactions these unit particles are merely rearranged, they are not destroyed. This is referred to as the **Law of Conservation of Matter.**

Summary of Dalton's Atomic Theory

1. All substances are composed of small, dense, indestructible particles called atoms.
2. Atoms of a given substance are identical in mass, size, and shape.
3. An atom is the smallest part of an element that enters into a chemical change.
4. Molecules of a compound are produced by the combination of the atoms of two or more different elements.

ELEMENTS

Matter is anything that occupies space. A **substance** is a distinct kind of matter consisting of the same properties throughout the sample. All matter is made up of **elements** (Chart 1-2). Elements are substances that cannot be broken down into other simpler substances by ordinary chemical means. There are 92 naturally occurring elements on Earth, each differing from the others by the number of protons in the nuclei of its atoms. These are referred to as *natural* elements. Examples of natural elements include iron (Fe), oxygen (O), mercury (Hg), copper (Cu), aluminum (Al), hydrogen (H), sodium (Na), gold (Au), silver (Ag), sulfur (S), and

carbon (C). Hydrogen (H) is the lightest element with only one proton in its nucleus while uranium (U) is one of the heaviest at 92. Currently, 113 total elements exist, including those that are man-made (*artificial* elements) with new ones periodically being synthesized.

Elements are composed of a single kind of atom; if it is composed of different atoms in a fixed ratio, it is referred to as a **compound.** Water (H_2O) is a compound composed of different atoms. It can be separated into simpler substances, thus it is not an element. It separates into two different gases, oxygen (O_2) and hydrogen (H_2), which are elements.
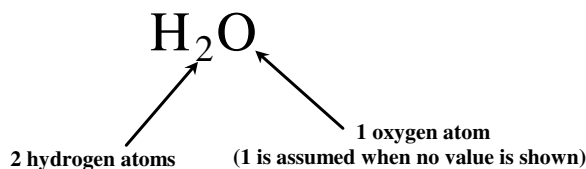
$$H_2O$$

2 hydrogen atoms

1 oxygen atom
(1 is assumed when no value is shown)

Table salt (NaCl) is also a compound composed of the elements sodium (Na) and chlorine (Cl). Table sugar or sucrose ($C_{12}H_{22}O_{11}$), is a compound formed from a combination of the three elements—carbon (C), hydrogen (H), and oxygen (O)— in a distinct ratio. Important characteristics of a compound are:

(a) Compounds are made from simpler substances called elements, and can be decomposed into elements by ordinary chemical means.

(b) The elements of which a compound is composed (its components) are com- bined in a definite proportion by mass. This proportion is the same in all samples of the compound.

(c) The chemical and physical properties of a compound are different from those of its components.

Of the more than 100 known elements, eight make up more than 98% of the Earth's crust [oxygen (O), silicon (Si), aluminum (Al), iron (Fe), calcium (Ca), sodium (Na), potassium (K), and magnesium (Mg)].

A **mixture** consists of two or more substances (elements or compounds) phys- ically mixed together but not chemically combined like in a compound. A **solution** (also called a mixture) with no visible differing parts (e.g., a single phase) is referred to as **homogenous.** Sugar dissolved in water produces a single phase ho- mogeneous mixture (or solution) of sugar water. A **heterogenous** mixture has vis- ibly different parts (or layers or phases). Most salad dressings, for example, have visible different parts no matter how thoroughly they are mixed and can be sepa- rated by ordinary physical means (Chart 1-2).

Metals and Nonmetals. Most elements fall into one of two groups—*metals* or *nonmetals* (refer to the Periodic Table inside the front cover of this book). Metals conduct heat and electricity readily and reflect light (have luster) (Table 1-2). Most metals are quite ductile (capable of being drawn into wires) and malleable (capable of being hammered into sheets). These properties exist because electrons in metals are continually exchanged between atoms and are not restricted to fixed positions.
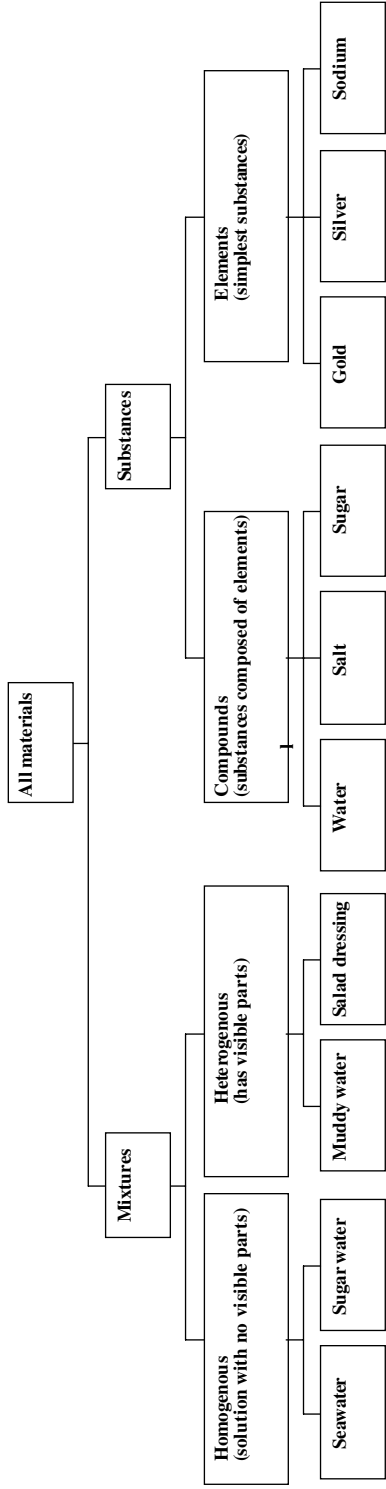
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                              All materials
                                   |
              ┌────────────────────┴────────────────────┐
          Mixtures                                  Substances
              |                                          |
      ┌───────┴───────┐                        ┌─────────┴─────────┐
  Homogenous      Heterogenous           Compounds             Elements
  (solution with  (has visible parts)    (substances composed  (simplest substances)
  no visible parts)                        of elements)
      |               |                        |                     |
  ┌───┴───┐       ┌───┴────┐          ┌────────┼────────┐   ┌─────────┼─────────┐
Seawater  Sugar  Muddy    Salad     Water    Salt    Sugar  Gold    Silver   Sodium
          water  water    dressing
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Chart 1-2. Classification of materials. Through chemical reactions, elements combine to form compounds. Through physical changes, substances are mixed to form mixtures.

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TABLE 1-2. Properties of Metals and Nonmetals

Metals	Nonmetals
Have a luster (shine)	Have low luster
Good conductors of heat	Poor conductors of heat
Good conductors of electricity	Poor conductors of electricity
Malleable (capable of being hammered into sheets)	Nonmalleable
Ductile (capable of being drawn into wire)	Nonductile (brittle)

This property is referred to as the ''sea of electron'' effect. Metals also have fewer electrons in their outer shells than nonmetals. Examples include copper (Cu), platinum (Pt), silver (Ag), aluminum (Al), mercury (Hg), magnesium (Mg), tin (Sn), zinc (Zn), and gold (Au).

Nonmetallic elements typically have opposite characteristics of metals. Nonmetals are generally lighter in weight than metals; they are brittle (not malleable); not ductile; vary in color; and are poor conductors of electricity and heat (Table 1-2). These properties are due to nearly complete or filled outer shells with electrons that are held relatively rigidly, and thus tend to be somewhat less reactive. Examples include sulfur (S), chlorine (Cl), carbon (C), nitrogen (N), and oxygen (O).

Except for the noble gases, no element in the free state possesses the stable, complete outermost shell. All elements with incomplete outer shells tend to combine with other elements and thereby undergo significant bonding under ordinary conditions. Therefore, the completeness of the outermost shell is a factor in determining bonding capacity of an element; that is, the ability of its atoms to combine with other atoms and will be discussed in further details later in this chapter.
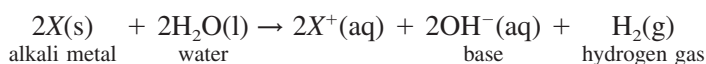
Naming Elements. Elements are often named after the discoverer. Different symbols are used to designate each different element. The symbol of an element is either the first letter of the name or the first letter followed by some significant other letter. The first letter of the symbol is always capitalized and the second letter (if used) is always lower case. For examples, the symbol of carbon is C; the symbol of calcium is Ca; the symbol of chromium is Cr; and, the symbol of cobalt is Co. The symbols of some elements are derived from languages other than English. For example, the symbol for gold, Au, is derived from the Latin word, *aurum*; sodium (Na) is from *natrium*; while iron has the symbol Fe, from *ferrum.*

Grouping Elements—The Periodic Table. One of the great milestones in chemistry's evolution was the arrangement of elements into groups with similar properties. The **Periodic Table** or chart shown on the inside front cover of this text illustrates this grouping of elements. In this table the metallic elements are located on the left side of the heavy line that runs diagonally across the table while the nonmetals are located to the right.

The periodic table is read like a newspaper, from left to right and down the page. Each horizontal row of the periodic table represents a **period** or **series.** An electron is added to the valence (outer) shell of the atoms of each element as one moves from left to right within each of the seven periods.

The vertical columns of elements in the periodic table are called **groups** or **families.** In older periodic tables, a Roman numeral and a capital letter were used to identify each group. Today, numbers from 1 to 18 are used to identify these. In general, elements in the same group have similar properties and have the same number and similar arrangement of outer-shell (valence) electrons. Each element is located within a square containing the symbol, relative atomic mass, and atomic number of that element. The elements in several of the groups have family names. These are:

Group IA (1), the Alkali (or Sodium) Family. These are highly reactive metals, silvery in color, with relatively low densities. They are easily oxidized (corroded) in air and react vigorously with water to form hydrogen gas and a class of compounds called **bases** (OH^-).

$$2X(s) \quad + \ 2H_2O(l) \rightarrow 2X^+(aq) + 2OH^-(aq) + \quad H_2(g)$$

$$\underset{\text{alkali metal}}{} \quad \underset{\text{water}}{} \qquad \qquad \underset{\text{base}}{} \qquad \underset{\text{hydrogen gas}}{}$$

where X represents any of the alkali metals (Group IA, or 1).

Due to this oxidation tendency, special storage techniques for these elements in their pure state or form are needed. Many are stored under light oil to keep air and moisture away. These atoms all have only one electron in the outermost shell. Hydrogen (H), sodium (Na), and potassium (K) are commonly used members of Group IA and their reactivity in this group increases from top to bottom of the group in the periodic table. Because of their great reactivity, the compounds they form are more important than the metals themselves, e.g., sodium chloride, sodium hydroxide, sodium carbonate, sodium silicate, and potassium chloride.

Group IIA (2), the Alkaline-earth (or Calcium) Family. These are also silvery metals which react with oxygen-forming oxides and acids to release hydrogen gas. Since the Group IIA (2) metals have two electrons in the outermost shell of their atoms, these are not as reactive as the alkali metals (Group IA, or 1). Like the alkali metals, the reactivity of the alkaline earth metals increases from top to bottom of the group in the periodic table. Magnesium (Mg) and calcium (Ca) are commonly used members of Group IIA. Mg is the lightest metal used for construction and Ca compounds are used as common liming sources.

Group IIIA (13). Aluminum (Al) is the major commercially important element of Group IIIA. Al is the most abundant metal in the Earth's crust, making up 8.3% by mass. Al-containing minerals, such as feldspars, weather to form clay, a major component of soil. Aluminum, of course, is also an important lightweight, corrosion-resistant metal used in many applications of modern life. Boron (B), another member of Group IIIA, is an important micronutrient needed in minor amounts for most plants.

Groups IIIB-IIB (3–12), the Transition Metals. These elements are metallic and include many common metals such as iron (Fe), copper (Cu), gold (Au), and silver (Ag). The oxidation states of these elements may vary depending on energy considerations. Most of the transition elements have more than one kind of ion – for

example, iron forms iron(II) ion, Fe^{+2}, and iron(III) ion, Fe^{+3}. Most of the transition metals also have high melting and boiling points and high densities and are hard and strong. Iron (Fe) has many manufacturing and construction uses, while gold is used in jewelry, dentistry, electronics, science, and as a monetary unit. Titanium(IV) oxide is a white-colored member of this group and is used as a white pigment in paint, a coating on paper, and as a filler in plastic and rubber.

Group VA (15), the Nitrogen Family. Nonmetallic members of this group are nitrogen (N) and phosphorus (P), while bismuth (Bi) is metallic, and arsenic (As) and antimony (Sb) have both metallic and nonmetallic (called *metalloids*) properties. The atoms of each of these elements have five electrons in the outer shell and a very stable inner shell. Nitrogen and phosphorus are two major nutrients for plants.

Group VIIA (17), the Halogen Family. Halogens, which means ''salt formers,'' are relatively reactive nonmetals. Seven electrons are found in the outer shells of the atoms of these elements. The reactivity of the halogens decreases from top to bottom of the group. At room temperatures, fluorine (F) and chlorine (Cl) are gases, bromine (Br) is a liquid, and iodine (I) and astatine (At) are solids. Iodine vaporizes easily and forms a violet gas that is highly corrosive. When in their elemental gaseous state, the halogens are found as diatomic (two-atoms) molecules, e.g., F_2, Cl_2, I_2, etc. All of these gases are considered poisonous. Chlorine is the most used halogen for bleach, to purify water, vinyl (plastic) production, and to manufacture other organic and inorganic chemicals. Fluoride is used to fight tooth decay, while iodine is a necessary micronutrient often added in commercial salt sources.

Group O (also referred to as Group 18 or VIII), the Noble Gases. They include helium (He), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn). These are nonmetals that rarely react with other elements, and are gases at room temperatures. These elements, with the exception of helium, have eight electrons (called an **octet**) in the outer shell, which is the largest number of electrons found in an outer shell, and therefore are virtually unreactive (very stable). Helium's (He) outermost shell (K or 1) is complete with two electrons (a pair), making it stable. When the outer shells are completely filled, the electrons shield, or screen, the positive charge of the nucleus, thus making it extremely difficult for such atoms to combine with others. As a result, the noble gases occur in nature as single atoms. The noble gases were referred to in the past as *inert gases* because they were thought to be chemically inert. However, in 1962 several of these have been made to react to some degree with fluorine and with oxygen. The lack of reactivity of helium and argon, the most common noble gases, is the basis for their main use—as an inert atmosphere for high-temperature processes such as arc welding. Although twice as dense as hydrogen, helium is also used to fill balloons and blimps since it is nonflammable.

Inner Transition Elements, the Lanthanides and Actinides. These are metallic elements listed in the two long rows beneath the table. Uranium (U) and plutonium (Pu) are generally the most widely recognized elements in this group. Almost all of the remaining elements have been synthesized in nuclear reactions and are characterized by their radioactivity and are not found naturally in the Earth's crust. Uranium and plutonium are used in nuclear power plants and in nuclear weapons.

Changes in Matter During Reactions

Chemical and physical changes occur in matter during reactions. Physical changes are those in which certain identifying properties of a substance remain. Examples are freezing, boiling, and dissolving. Chemical changes are those in which different substances with new properties are formed. Reactions that absorb energy as they proceed are **endothermic.** Reactions that liberate energy are **exothermic.** The rates of some chemical reactions can be accelerated by a **catalyst,** which is a substance that speeds up or slows down a chemical reaction without itself being consumed.

In nature, a basic tendency is for processes to occur that lead to a lower energy state. Another basic tendency is for processes to occur that lead to a more disordered or more random state. **Entropy** is the property that describes the disorder of a system. The more disordered the system, the higher its entropy.

Atomic Structure

Electrical forces hold the nuclei and electrons together in an atom. Each electron carries a unit of negative electrical charge, and each proton has an equal sized unit of positive electrical charge. Neutrons carry no charge. The net positive charge of the nucleus is offset by electrons. The electrons of an atom are not distributed uniformly around the nucleus, nor are they distributed randomly. They occupy certain regions of space determined by their energy, usually referred to as **orbits, shells,** or **energy levels.** These orbits can contain a fixed number of electrons. This arrangement of a nucleus and its electrons is referred to as the **atomic structure** (Figure 1-2). Electrons found at different distances from the nucleus have different energies. This ring model helps visualize the energy levels of an atom, helps keep track of the number of electrons in each energy level, and shows how atoms are likely to interact.

Electrons move about the nucleus with different energies. Electrons fit only into specific orbitals and energy levels around the nucleus, and depending upon this energy, some arrangements are more stable than others. This arrangement is similar to an orbiting satellite around the earth except gravitation forces hold a satellite in orbit, whereas electrical attraction of oppositely charged particles holds electrons in an atom. The somewhat random orbiting pattern of electrons is also synonymous to the random flight pattern of bees around a bee hive where no two bees fly exactly the same pattern but overall circle the hive in varying shaped orbits.

An atom is most stable when all of its electrons are at their lowest possible energy levels (called its **ground state**); in other words, closest to the nucleus. However, the attraction between an electron and a nucleus turns into a repulsive force if they approach too close. This repulsion keeps the electrons and nuclei from colliding. The atoms remain stable when the attraction between nuclei and electrons is sufficient to overcome the forces of repulsion.

Orbital Designation

Shells or Energy Levels. Seven principal shells are known and are designated numerically 1 through 7 or previously, alphabetically as K, L, M, N, O, P, and Q. Although seven shells exist, most elements involved in the plant sciences have only four. In the order listed, the letters (or numbers) represent increasingly greater

distances from the nucleus and, therefore, higher energy levels. The electrons of an atom fill the energy levels (or shells) in order: the first is filled before the second, the second before the third, and so on. Each shell surrounding the nucleus can accommodate only a fixed number of electrons. The simplest atom, hydrogen, has a single electron that moves around the nucleus in the first energy level, while helium has two (Figure 1-3). Atoms with more than two electrons must have at least two shells to hold these. The first shell (designated as 1 or K) can hold only two electrons, and the second (designated as 2 or L), eight (Table 1-1). Every outer shell similarly can hold no more than eight electrons, except with unusual elements. Eight electrons in an outermost shell is extremely stable and is referred to as an **octet.**

Since the first energy level for most elements is filled by two electrons, additional electrons must occupy higher energy shells, farther from the nucleus. The second
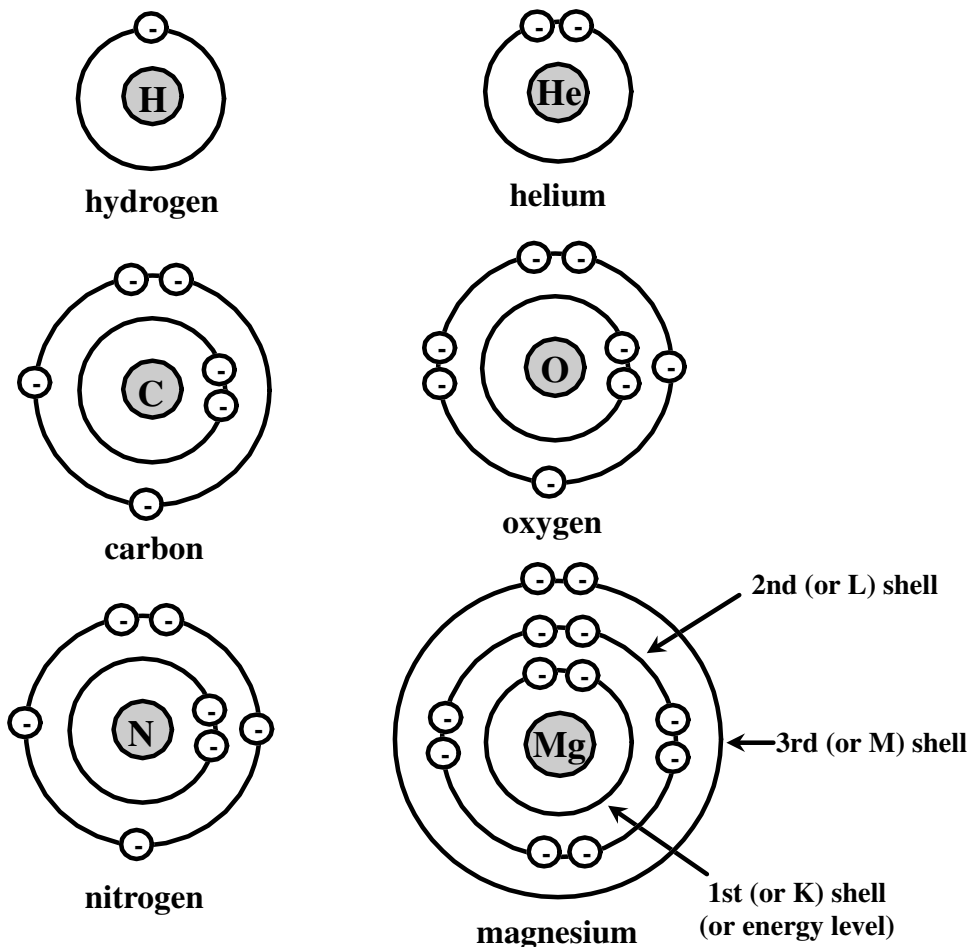
Figure 1-3. Electron configurations for the atoms of several elements found in biology. Refer to Table 1-1 for the number of electrons per shell for each element.

energy level can hold up to eight electrons, and so can the third energy level of elements through atomic number 20 (calcium). Carbon, nitrogen, and oxygen nuclei have six, seven, and eight protons, respectively (Table 1-1), and they exert a much stronger attraction for electrons than hydrogen. In the atom of sodium, for example, 11 electrons occur, two in the first shell, eight in the second, and one electron in a third (designated as 3 or M) shell. For elements of higher atomic number than 20, the pattern becomes more complex.

The outermost principal energy level of any atom is called the **valence shell.** The electrons in this outer shell are called **valence electrons.** The chemical nature of an element depends largely on the number of valence electrons, which varies from 1 to 8. Refer to Appendix A for additional information on electron (or orbital) pairs.

Electrons and Energy. The distance between an electron and the nucleus around which it moves is determined by the electron's potential energy, or *energy of position.* The more energy an electron has, the farther it moves from the nucleus. Thus an electron with a relatively small amount of energy is found close to the nucleus and is said to be at a low energy level. An electron with more energy is farther from the nucleus, at a higher energy level. With a sufficient input of energy, an electron can move from a lower to a higher energy level, but not to an energy state somewhere in between. An atom that has absorbed sufficient energy to boost an electron to a higher energy level is said to be in an *excited state.* As long as the electron remains at the higher level it possesses the added energy. When it returns to the lower energy level (or *decays*), as it tends to do, the added energy (often as radiation) is released. The most stable state of an atom is called its *ground state* and has this lower energy.

Isotopes. Although all atoms of a particular element have the same number of protons in their nuclei, atoms of the element may contain different numbers of neutrons. These different forms of the same element, differing in atomic weight (number of neutrons) but not in atomic number (a.k.a., number of protons), are known as **isotopes** (*iso*—meaning "same"). For example, the most common isotope of hydrogen may be shown using the symbol ^{1}H. This isotope contains one proton and no neutrons in the nucleus. The total number of protons and neutrons is shown as a superscript. Deuterium (or heavy hydrogen, ^{2}H) is another isotope of hydrogen that contains one proton and one neutron. Tritium (^{3}H) is a third hydrogen isotope that contains one proton and two neutrons (Figure 1-4). The atomic weight of an element having two or more isotopes is a weighted average value calculated for the naturally occurring mixture of isotopes.

Some isotopes (for example, tritium, ^{3}H) are *radioactive.* This means the nucleus is unstable and emits energy as it changes (or decays) to a more stable form. The energy (particles or rays) released by **radioactive isotopes** (also called **radioisotopes**) can be detected by various means, such as with a Geiger counter or on photographic films. The rate of decay of a radioisotope is measured in terms of **half-life,** which is the time in which half the atoms in a sample lose their radioactivity and become stable. Half-lives vary widely; for example, the radioactive nitrogen isotope ^{13}N has a half-life of 10 minutes while tritium (^{3}H) has a half-life

	Hydrogen	Deuterium	Tritium

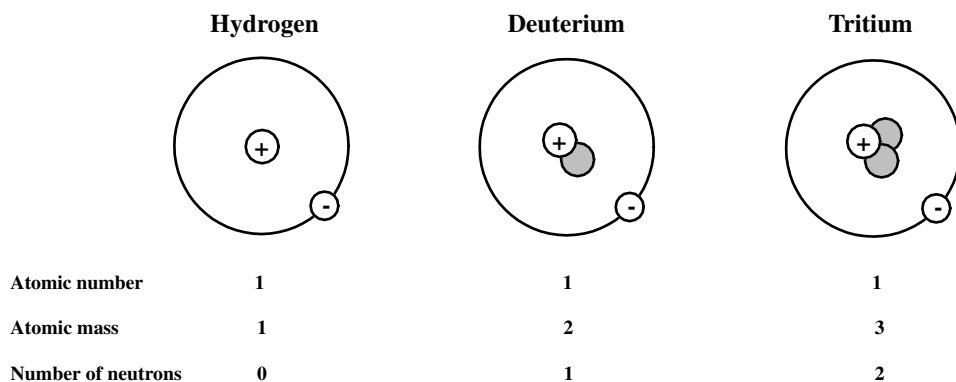|	Hydrogen	Deuterium	Tritium
Atomic number	1	1	1
Atomic mass	1	2	3
Number of neutrons	0	1	2

Figure 1-4. The three isotopes of hydrogen differ due to the number of neutrons. Since they have the same number of protons, the three isotopes have the same atomic number. Neutrons only cause atoms to acquire additional electrons to move at similar speeds.

of over 12 years. For certain radioactive elements, their half-lives are quite long. For example, uranium 238's half-life is 4.5×10^9 (or 4,500,000,000) years, which causes a major problem in handling and disposal of its radioactive ''waste.''

Radioisotopes are widely used in biological research. They are used to *date,* or determine the age of fossils. They are also used as *tracers* to trace or follow the course of many essential chemical reactions in living systems. For example, radioactive carbon dioxide ($^{14}CO_2$) was used to elucidate the pathways of photosynthesis, since isotopes of an element, ^{14}C in this case, have the same chemical properties as the nonradioactive isotope. Isotopes are also used in **autoradiography,** a technique where a sample of material containing a radioisotope is exposed to a sheet of photographic film. Energy emitted from the isotope leaves traces on the film and so reveals the exact location of the isotope within the specimen. Herbicides containing radioactive carbon are often applied to plants, and the treated plant is then exposed at various timings to photographic film to determine the uptake and translocation properties of the herbicide within the plant.

The Basis of Chemical Reactivity

Atoms react by losing, gaining, or sharing electrons. The manner in which an atom reacts chemically is determined by the number and arrangement of its electrons. As discussed, an atom is most stable when all of its electrons are at their lowest possible energy level. Moreover, an element having atoms with a completely filled outermost energy level is more stable than an element having atoms with a partially filled outer energy level. Oxygen, for example, requires eight electrons to achieve a neutral charge. Two of these are in the inner shell and six are in the outer shell. Oxygen, therefore, needs to gain two electrons to stabilize its outer shell to eight. This gain of electrons, thus attaining a more negative oxidation state, is called **reduction.** Magnesium (Mg) has two electrons in its outer shell. When Mg loses these two electrons, its outer shell contains eight electrons and the resulting ion has an excess positive two charge. The loss of electrons, thus attaining a more

positive oxidation state, is called **oxidation.** In another example, helium (atomic number 2), neon (atomic number 10), and argon (atomic number 18) have completely filled outer energy levels and so tend to be unreactive. This also results in equal numbers of electrons and protons, so the atoms are electrically neutral.

The outermost shell of electrons, called the **valence shell,** determines the chemical behavior of most elements. The Lewis Dot system is often used to simplify electron structures of atoms and allows for visualizing where the electrons are lost, gained, or shared by different atoms in the formation of compounds or molecules. It is often diagramed as a dot system when writing chemical structures and equations to indicate the number of only the valence (outer shell) electrons. The symbol of the element is used and the electrons (designated as dots) are distributed along the two vertical and two horizontal surfaces of an imaginary square. Begin at the top and proceed clockwise. Distribute the first four dots around the chemical symbol before putting two dots next to each other. This essentially conforms to four orbitals which can each contain a maximum of two electrons and thus, accommodate all the eight valence electrons needed for chemical stability. All the elements in the same group of the Periodic Table have the same notation since they all have the same number of outermost electrons. For example, the Lewis Dot diagram for a sodium atom is the same as that for a lithium atom and the diagram for an oxygen atom is the same as that for a selenium atom as they are both members of group VIA (or 16). The Lewis symbols of the first 20 elements of the periodic table are shown below.
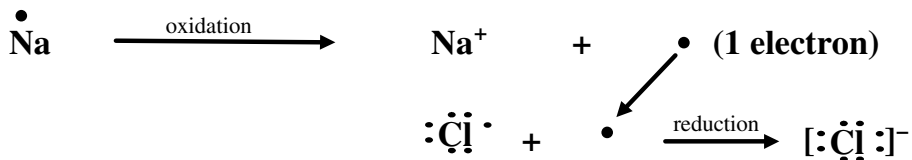

Ground State
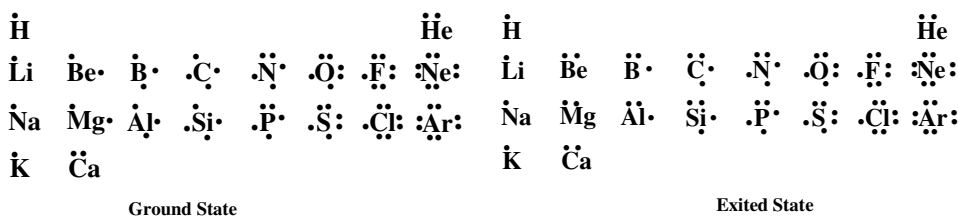
Exited State

In their ground state or unexcited state, electrons usually pair up. However, in their excited state, electrons are unpaired where possible as shown.

The Lewis Dot system indicates the number of electrons that can be lost, gained, or shared. There are two possible structures for carbon, which accounts in part for the large number of carbon compounds possible. The number of bonds that an element usually forms in compounds equals the number of unpaired electrons. For example, H can form 1 bond, Be—2, B—3, C—4, N—3, O—2, F—1, and Ne—0.
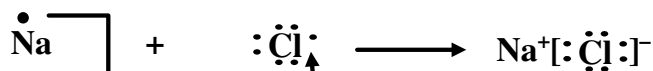
A simple method of producing Lewis Dot symbols in the excited state is to place one dot representing a valence electron on each side or face of an imaginary square if four electrons are available. If not, place only the number of valence electrons available. If there are more than four electrons, start pairing them up on the faces.

Electron transfer using the Lewis Dot system for formation of ionic compounds can be demonstrated for the formation of sodium chloride (table salt):

Example:

$$\overset{\bullet}{Na} \xrightarrow{\text{oxidation}} Na^+ \quad + \quad \bullet \text{ (1 electron)}$$

$$:\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}\cdot \quad + \quad \bullet \xrightarrow{\text{reduction}} [:\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}:]^-$$

The ionic compound formed (NaCl, sodium chloride or table salt) would be shown using the Lewis Dot system as:

$$\overset{\bullet}{Na} \quad + \quad :\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}: \longrightarrow Na^+[:\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}:]^-$$

The formation of sodium chloride also represents an oxidation-reduction reaction since sodium loses an electron (is oxidized), while chlorine gains this electron (is reduced).

In atoms of most elements the outer energy level is only partially filled, which is an unstable arrangement. These atoms tend to interact with other atoms in such a way that, after reaction, both atoms have completely filled outer energy levels. Some atoms lose electrons while others gain electrons. Sodium has an atomic number of 11, which represents two electrons in its inner shell, eight in its second shell, and one in its third shell. As a consequence, the sodium atom has a tendency to lose this odd electron (or become oxidized), achieving a stable electron configuration of eight in what then becomes its outer shell. The loss of this electron gives sodium a net positive charge of 1. Using chemical symbols, an atom of sodium is represented as Na and a sodium ion which has been oxidized is Na^+. Chlorine, with an atomic number of 17 and 7 electrons in its outer shell, needs to gain one electron in order to stabilize its outer shell to 8. In gaining an electron, the Cl atom acquires a negative charge (is reduced) and becomes Cl^-.

lose 1 electron (oxidation)		gain 1 electron (reduced)	
Na $\longrightarrow$	Na^{+1}	Cl $\longrightarrow$	Cl^-
sodium atom	sodium ion	chlorine atom	chloride ion
or		or	
Na + energy $\longrightarrow Na^{+1}$ +	$1e^-$	Cl + $1e^- \longrightarrow Cl^-$ +	energy

It may be easier to visualize this process by actually counting the number of electrons and protons during an oxidation-reduction reaction. For example, a magnesium (Mg) atom has 12 electrons and protons. During oxidation it loses 2 electrons
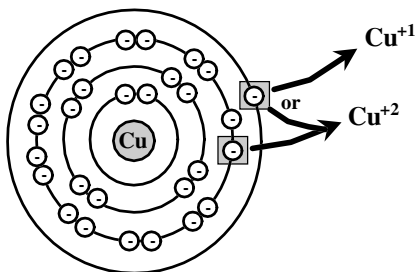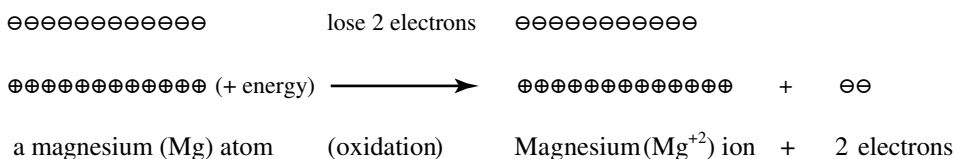
Figure 1-5. The normal electron structure of the copper atom is 2-8-18-1, resulting in an oxidation value of +1. However, an electron from the next-to-outermost shell (designated as the 3 or M shell) can also act as a valence electron, thus giving the atom an oxidation charge of +2.

from its outer shell and has two more protons than electrons. The magnesium ion then has a net 2 positive charge and is indicated by the symbol Mg^{+2}.
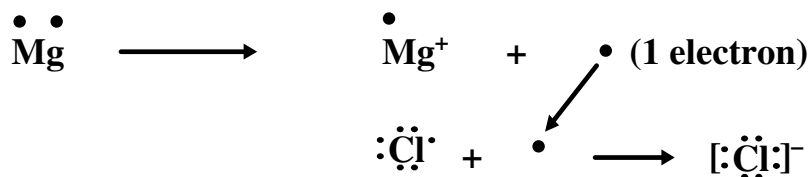
ⵔⵔⵔⵔⵔⵔⵔⵔⵔⵔⵔⵔ   lose 2 electrons   ⵔⵔⵔⵔⵔⵔⵔⵔⵔⵔ

⊕⊕⊕⊕⊕⊕⊕⊕⊕⊕⊕⊕ (+ energy) $\longrightarrow$ ⊕⊕⊕⊕⊕⊕⊕⊕⊕⊕⊕⊕   +   ⵔⵔ

 a magnesium (Mg) atom   (oxidation)   Magnesium (Mg^{+2}) ion   +   2 electrons

  The number of electrons an atom or molecule must gain or lose to attain a stable configuration in its outer shell is its **oxidation state** which in the past was referred to as its **valence** (Table 1-1). From the examples above, magnesium ions (Mg^{+2}) have an oxidation state (or valence) of $^{+}2$ because it has lost two electrons, and chlorine ions (Cl^{-}) have an oxidation state (or valence) of $^{-}1$ because it has gained one electron.

  Some metallic elements may have more than one oxidation state (or valence). Such elements are heavier atoms that have three or more filled shells and in which an electron may move from one shell to another. Iron (Fe), for example, can have a charge of $^{+}2$ or $^{+}3$ depending on the energy available in the reaction while copper (Cu) may have a charge of $^{+}1$ or $^{+}2$ (Figure 1-5). Copper not only has only one electron in its outermost (valence) shell, it also has loosely bound electrons in the next-to-outermost shell. This loosely bound electron can move to the outer shell and when combined with certain elements, copper gives up one electron, forming Cu^{+} (formerly called cupr*ous*). While with other elements, higher energy in the reaction is necessary for an additional electron loss and copper gives up two electrons, forming Cu^{+2} (formerly called cupr*ic*). This is an important property in its biological activities.
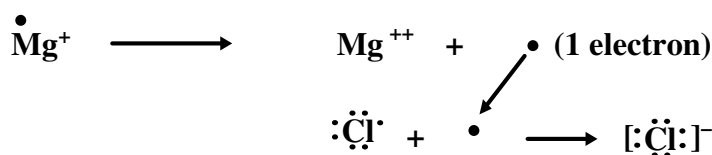
 Example:

 The formation of magnesium chloride required 2 chlorine ions for each magnesium ion:
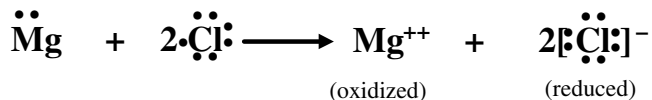
Step 1:

$$\overset{\bullet\ \bullet}{Mg} \longrightarrow \overset{\bullet}{Mg^+} \ + \ \bullet \text{ (1 electron)}$$

$$:\overset{\bullet}{\underset{\bullet\bullet}{Cl}}\bullet \ + \ \bullet \ \longrightarrow \ [:\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}:]^-$$

Step 2:

$$\overset{\bullet}{Mg^+} \longrightarrow Mg^{\,++} \ + \ \bullet \text{ (1 electron)}$$

$$:\overset{\bullet}{\underset{\bullet\bullet}{Cl}}\bullet \ + \ \bullet \ \longrightarrow \ [:\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}:]^-$$

Chlorine, in nature, is found as a diatomic molecule (Cl_2) which requires two electrons from Mg to form magnesium chloride ($MgCl_2$). The loss/gain of electrons may be summarized as shown:

$$\overset{\bullet\bullet}{Mg} \ + \ 2\bullet\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}\bullet \longrightarrow Mg^{++} \ + \ 2[:\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}}:]^-$$
$$\qquad\qquad\text{(oxidized)}\qquad\qquad\text{(reduced)}$$

This leads to a foundation for writing formulas for compounds.

Some of the chemical elements have a higher affinity for their electrons than others. These elements have a tendency to share their electrons with other atoms rather than give up or accept electrons in order to obtain an octet or complete outer shell. This sharing results in the formation of molecules or compounds that are covalently bonded. Hydrogen (H^+) is one such element along with oxygen, nitrogen, and members of the halogen family (members of vertical column VII-A [or 17] on the periodic table). These elements share electrons with unpaired electrons of other elements as well as with like atoms.

The gaseous elements on the periodic table with the exception of the noble gases form covalent bonds in this manner with atoms of their own kind. This results in the formation of diatomic molecules (2-atom molecules). These gases are found in this molecular configuration in nature (H_2, O_2, F_2, etc.).

Example:

Lewis dot structures for several covalent molecules:

F_2 $\ddot{\underset{..}{F}} \! : \! \ddot{\underset{..}{F}} :$ or   **F–F** NH_3 **H** $: \underset{..}{\overset{..}{N}} :$ **H**   or   **H–$\underset{..}{N}$–H**
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad$ **H** $\qquad\qquad\qquad$ **H**

HF   **H** $: \ddot{\underset{..}{F}} :$ or   **H–F** H_2O $: \overset{..}{\underset{..}{O}} :$ **H**   or $: \overset{..}{O}$ **–H**
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad$ **H** $\qquad\qquad\qquad$ **H**
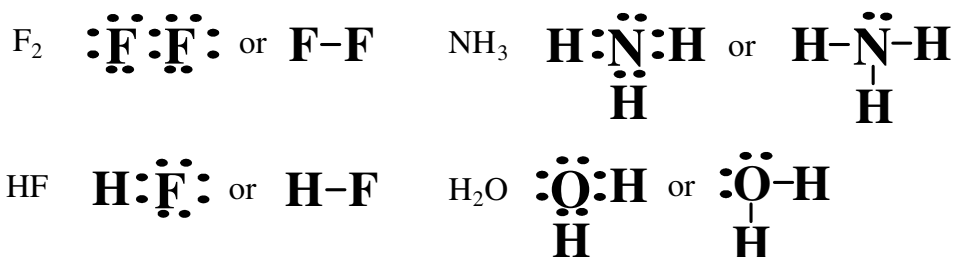
The electron-dot structure can be used to indicate shared electrons; however, chemists frequently use a dash (–) such as shown above for water (H–O–H) and other molecules. This dash represents a pair of shared electrons. This type of formula is called a *structural formula,* while the *molecular formula* (e.g., H_2O for water) indicates only the actual composition (ratio) of atoms in the molecule.

Electronegativity. The atomic nuclei of different elements have different degrees of attraction for electrons in their chemical bond. The affinity of an element for electrons to move to the most stable possible configuration in a covalent bond is known as its **electronegativity.** Since an element that gains electrons is acting as an oxidizing agent (gains electrons), electronegativity is also a measure of the oxidizing strength of an element. Atoms having high ionization energies and high electron affinities, that is, atoms that lose electrons with difficulty and gain electrons readily, are very electronegative. Electronegativity is expressed on a scale of 0 to 4, with helium and other noble gases having electronegativity of 0 and fluorine having an electronegativity of 4 (Table 1-1). In the periodic table, electronegativities for elements increase from the bottom of the table to the top and from left to right. Fluorine (F) in the upper right-hand corner in the periodic table, for example, is a stronger oxidizing agent than any other element.
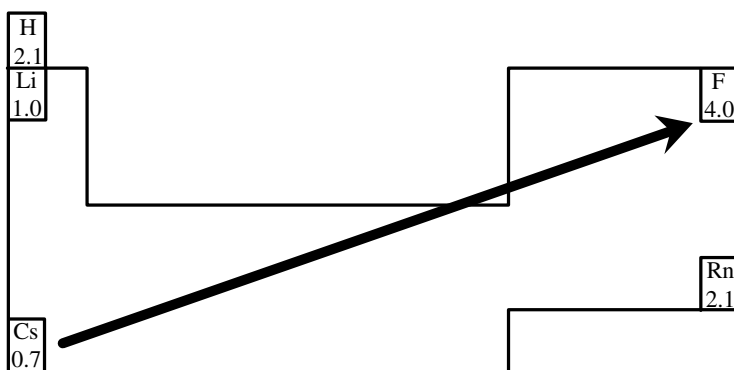
Electronegativity of the elements increase from bottom left of the periodic table to the upper right. Fluorine (F), in the upper right-hand corner, is a stronger oxidizing agent than any other element.

A higher value means a stronger tendency to retain the electrons, that is, the more polar (has a slightly positive and negative region) the bond becomes. Differences in electronegativity between two atoms can identify the nature of the chemical bond, whether a bond is more ionic or more covalent. The shorter distance between the nucleus and outer shell electrons causes this greater affinity. For example, a molecule with a mixture of nuclei tends to be negative near the nitrogen and oxygen nuclei, and positive near the carbon, hydrogen, phosphorus, and sulfur nuclei. With water (H_2O), the hydrogen of one water molecule is attracted to the oxygen of the neighboring water molecule because of their slightly opposite charges. The resulting hydrogen bond gives water many unique properties such as being a universal solvent, having high surface tension, and having relatively high boiling and low freezing points that render it readily available for earthly processes.

When writing formulas, the element furthest to the left in the periodic table (less electronegative) is usually written on the left side of the formula. If two elements are from the same group, the one lower in the column in the periodic table is usually written first. Note: notable exceptions include methane (CH_4) and ammonia (NH_3).

IONS, MOLECULES, AND CHEMICAL BONDS

Except for the noble gases such as He, Ar, Kr, Xe, and Rn, no element in the free state possesses the stable, complete outermost shell. The noble gases are not assigned values because of their relative inertness since their outer shells are complete. Elements with incomplete outer shells tend to combine with other elements and thereby undergo significant bonding. Most elements found in the Earth's crust are in a combined state. The abundance of oxygen primarily accounts for this. Therefore, the completeness of the outermost shell is a factor in determining bonding capacity of an element; that is, the ability of its atoms to combine with other atoms. Only a few metals such as gold (Au) and silver (Ag) are found in a free state in nature.

All atoms are electrically neutral since they have an equal number of positive protons and negative electrons. Atoms can interact to achieve completely filled outer energy levels in different ways—by losing electrons, by gaining electrons, or by sharing electrons with each other. The gain or loss of electrons produces charged atoms, called **ions** (from a Greek word meaning ''to go''). An ion is an atom or group of atoms that carries an electrical charge. Ions are symbolized with a superscript to indicate the number and sign of the excess charges. For example, K^+ indicates the potassium ion with one more proton than the number of electrons; the oxygen ion, O^{-2}, has two more electrons than protons. The charge carried by an ion determines how many oppositely charged ions are combined with it in a compound. **Cations** are positively charged ions (for example, K^+) while **anions** are negatively charged ions (for example, O^{-2}). The sharing of electrons produces new, larger particles called **molecules,** which are assemblies of atoms held together by chemical bonds. **Diatomic** molecules contain two atoms including many of the gaseous elements such as hydrogen (H_2), oxygen (O_2), nitrogen (N_2), and chlorine (Cl_2). Some elements such as neon (Ne), argon (Ar), and helium (He) are unreactive under normal conditions. They do not combine with each other or with other ele-

ments and consist of only one atom. These are referred to as **monatomic.** The elements sulfur (S), and phosphorus (P) occur as multiatomic molecules in nature, e.g., S_8, P_4, etc.

When an ion is composed of more than one kind of atom, it is called a **polyatomic ion.** For example, a sodium ion (Na^+) is a cation, a chloride ion (Cl^-) is an anion, while a sulfate ion (SO_4^{-2}) is a polyatomic ion because it consists of sulfur (S) and oxygen (O) molecules. The charge carried by an ion determines the ratio in which it combines with other ions. A list of common positive and negative ions is found in Table 1-3. As mentioned earlier, some elements, such as iron (Fe), can exhibit more than one oxidation state (or charge) such as Fe^{+2} and Fe^{+3}.

When different elements combine or mix in a definite and constant proportion and are held together by chemical bonds, the product is a **chemical compound.** Examples of chemical compounds are water (H_2O), table salt or sodium chloride (NaCl), carbon dioxide (CO_2), and glucose ($C_6H_{12}O_6$). The formula of a chemical compound consists of the symbols of the chemical elements involved and subscripts indicate the number of each element. The subscript one ($_1$) is not used since the symbol represents one atom. For glucose, its chemical formula, $C_6H_{12}O_6$, indicates six atoms each of carbon (C_6) and oxygen (O_6) and 12 atoms of hydrogen (H_{12}). For copper sulfate, $CuSO_4$, the formula shows that this compound has the proportions of one copper (Cu) atom, one sulfur (S) atom, and four oxygen (O_4) atoms.

Writing Chemical Formulas

When writing chemical formulas, the first step is to recognize the symbols of the elements in the compound. These can be found in tables such as Table 1-3. From this, the ion notations (including their charges) are written in the order named. The number of each kind of ion is then adjusted to provide a net total positiveness (valence $\times$ subscript) and negativeness (valence $\times$ subscript) charges of equal but opposite magnitude. This is referred to as assigning oxidation numbers (see box). For example, sodium chloride (NaCl) is represented by positively charged sodium ions, Na^+, and negatively charged chloride, Cl^- ions. When writing formulas for ionic compounds, the total charge of the first element (valence $\times$ subscript) must be equal and opposite the total charge (valence $\times$ subscript) of the second ion found in the compound. For sodium chloride, the charge of one sodium ion is equal ($^+1$) and opposite the charge of one chloride ion ($^-1$).

For polyatomic ions containing oxygen, these have four different forms and remembering the -*ate* form of each eliminates memorization of the other three. Some of the more common polyatomic ions include chlo*rate,* ClO_3^-, sulf*ate,* SO_4^{-2}; carbon*ate,* CO_3^{-2}; nit*rate,* NO_3^-; phosph*ate,* PO_4^{-3}; and bo*rate,* BO_3^{-3}. Oxidation numbers involving these and other ions will be discussed later.

Using the Periodic Table to Determine Oxidation Numbers. When using the periodic table, some general rules can be followed.

1. The algebraic sum of oxidation numbers (total charges) of all atoms in a formula is always zero.
2. The oxidation number in the periodic table for Groups IA (or 1) = $^+1$; IIA (2) = $^+2$; and, IIIA (B and Al only) = $^+3$. F = $^-1$. For example,

TABLE 1-3. Some Common Cations (Positively Charged Ions) and Anions (Negatively Charged Ions)

+1	Name	+2	Name	+3	Name	+4	Name
NH_4^{+}	ammonium	Ba^{+2}	barium	Al^{+3}	aluminum	Ce^{+4}	cerium(IV)
Cu^{+}	copper(I)	Cd^{+2}	cadmium	As^{+3}	arsenic(III)	Ni^{+4}	nickel(IV)
H^{+}	hydrogen	Ca^{+2}	calcium	Ce^{+3}	cerium(III)	Sn^{+4}	tin(IV)
Li^{+}	lithium	Cr^{+2}	chromium(II)	Cr^{+3}	chromium(III)	Ti^{+4}	titanium
Hg^{+}	mercury(I)	Co^{+2}	cobalt(II)	Co^{+3}	cobalt(III)		
K^{+}	potassium	Cu^{+2}	copper(II)	Fe^{+3}	iron(III)		
Na^{+}	sodium	Fe^{+2}	iron(II)	Ni^{+3}	nickel(III)		
Ag^{+}	silver	Pb^{+2}	lead(II)	Au^{+3}	gold(III)		
Au^{+}	gold(I)	Mg^{+2}	magnesium				
		Hg^{+2}	mercury(II)				
		Ni^{+2}	nickel(II)				
		Sn^{+2}	tin(II)				
		Zn^{+2}	zinc				

−1	Name	−2	Name	−3	Name	−4	Name
$C_2H_3O_2^{-}$	acetate	CO_3^{-2}	carbonate	AsO_4^{-3}	arsenate	$Fe(CN)_6^{-4}$	ferrocyanide
HCO_3^{-}	bicarbonate	CrO_4^{-2}	chromate	AsO_3^{-3}	arsenite	$P_2O_7^{-4}$	pyrophosphate
HSO_4^{-}	hydrogen sulfate	$Cr_2O_7^{-2}$	dichromate	BO_3^{-3}	borate	SiO_4^{-4}	orthosilicate
HS^{-}	hydrogen sulfide	O^{-2}	oxide	PO_4^{-3}	phosphate		
Br^{-}	bromide	O_2^{-2}	peroxide	$Fe(CN)_6^{-3}$	ferricyanide		
Cl^{-}	chloride	SO_4^{-2}	sulfate	N^{-3}	nitride		
ClO_3^{-}	chlorate	S^{-2}	sulfide				
ClO_2^{-}	chlorite	SO_3^{-2}	sulfite				
CN^{-}	cyanide	$S_2O_3^{-2}$	thiosulfate				
F^{-}	fluoride	HPO_4^{-2}	monohydrogen phosphate or biphosphate				
OH^{-}	hydroxide						
NO_3^{-}	nitrate						
NO_2^{-}	nitrite						
MnO_4^{-}	permanganate						
SCN^{-}	thiocyanate						
$H_2PO_4^{-}$	dihydrogen phosphate						

$$Na = +1 \text{ from IA (or1)}$$

$$Mg = +2 \text{ from IIA (or 2)}$$

$$Al = +3 \text{ from IIIA (or 3)}$$

Elements in IVA (or 4) do not always comply with the above statement. The values of $+4$ or -4 should be considered but there are many exceptions. Group VA (15) is usually $+3$, -3, or $+5$; Group VIA (16) is usually -2; Group VIIA (17) is usually -1.

3. $H = {}^{+}1$ except in binary compounds with metals where $H = {}^{-}1$, such as with NaH where $H = {}^{-}1$.
4. $O = {}^{-}2$. Nonmetals in group VA to VIIA (5 to 7) usually have negative values because they accept electrons. These elements can also share electrons. When writing formulas, the value of the Roman numeral above the group can be subtracted from 8 (8 electrons complete the outer valence shell) to determine the magnitude of the negative charge. For example,

$$F = -1 \text{ from VIIA (or 7)}$$

$$O = -2 \text{ from VIA (or 16)}$$

$$N = -3 \text{ from VA (or 5)}$$

Another reason to determine oxidation numbers of a substance is because an increase in acidity is common with increasing oxidation numbers. For example, the sulfur in sulfuric acid, H_2SO_4, has an oxidation number of $+6$ and is a stronger acid than the sulfur in sulfurous acid, H_2SO_3, which has an oxidation number of $+4$.

Example:

Which is the stronger acid,

a. HNO_3 or HNO_2?

oxidation number of each element	+1	?	−2		+1	?	−2
formula	H	N	O_3		H	N	O_2
total oxidation number of each element	+1	+?	−6 = 0		+1	+?	−4 = 0
		? = +5				? = +3	

For N in HNO_3; $+1 +? -6 = +5$ and for HNO_2; $+1 +? -4 = +3$; therefore, HNO_3 has a higher oxidation state for its N ($+5$) than in HNO_2 ($+3$), which indicates HNO_3 is the stronger acid.

b. $HClO_3$ or $HClO_4$?

oxidation number of each element	+1	?	−2		+1	?	−2
formula	H	Cl	O_3		H	Cl	O_4
total oxidation number of each element	+1	+?	−6 = 0		+1	+?	−8 = 0
		? = +5				? = +7	

$HClO_4$ has a higher oxidation for its Cl (+7) than in $HClO_3$ (+5), which indicates $HClO_4$ is the stronger acid.

Determining Formulas from Names. Knowing oxidation numbers also can be used in writing chemical formulas from names. For example, with lead(IV) oxide, the Roman numeral IV indicates an oxidation number of +4 for the lead (Pb) in this compound. Since the sum of oxidation numbers must equal zero, the sum of oxygen in lead(IV) must equal −4. According to rule 4 for assigning oxidation numbers, the oxidation number of oxygen is −2, thus two oxygen atoms are present to total zero, leaving,

$$+4 \text{ (from lead(IV))} + [2 \times -2 \text{ (from oxygen)}] = 0$$

Therefore, the formula for lead(IV) oxide is PbO_2.

Example:

Determine the formula of the following compound names:

a. **Lithium chlorite.** From the assigning oxidation rule 2, lithium is a member of the IA periodic group, thus has an oxidation value of +1. From rule 4, oxygen has a −2 value. Therefore, to algebraically equal zero, +1 (from lithium) + −2 (from oxygen) leaves +1 for chlorine, $LiClO_2$. Alternatively, from Table 1-3, chlorite is shown to be ClO_3^-, thus requires a +1 oxidation value from one lithium (Li) ion to sum zero.

b. **Sodium sulfite.** From Rule 1, IA group members, such as sodium, have a +1 oxidation value. From Table 1-3, sulfite is SO_3^{-2}. To algebraically equal zero, two sodium (+1) ions are needed for the −2 value from sulfite (SO_3^{-2}), and the formula is Na_2SO_3.

c. **Aluminum sulfate.** From Table 1-3, sulfate is SO_4^{-2} and from Rule 2, aluminum (Al) is +3. Since these do not sum zero (+3 + −2 ≠ 0), the lowest common denominator for 2 and 3 is needed which is 6. Therefore, the aluminum oxidation value equals +6 and the SO_4 is −6. To accomplish this, two Al ions are needed (2 × $^+3$ = $^+6$) and three SO_4 ions are needed (3 × −2 = −6), thus the formula is $(Al)_2(SO_4)_3$.

d. **Potassium nitrate.** From Table 1-3, nitrate's formula is NO_3^- and from Rule 2, potassium's oxidation value is +1. Since these sum zero (+1 from K + −1 from NO_3^- = 0), the formula is KNO_3.

When compounds are composed of ions that are not equally charged, these compounds must be adjusted so that the algebraic sum of the oxidation numbers is equal to zero. For example, calcium chloride, $CaCl_2$, is composed of the calcium (Ca^{+2}) ion and chloride (Cl^-) ions. For the algebraic sum of the ions to be equal to zero, two chloride ions are needed for each divalently charged calcium ion. The subscript '$_2$' indicates two chloride ions are needed for one calcium ion in calcium chloride. No subscript is required for Ca since only one Ca^{+2} ion is represented in the formula $CaCl_2$ and when this occurs, the symbol represents one atom and eliminates the need for the subscript$_1$.

For more complex compounds consisting of polyatomic ions, parentheses are used around the ion and subscripts are placed outside and to the right to indicate more than one ion. For example, a common fertilizer, ammonium sulfate, is composed of two polyatomic ions—ammonium, NH_4^+, and sulfate, SO_4^{-2}. In order for the $+$ and $-$ charges to be equal, two NH_4^+ ions are required for each SO_4^{-2} ion. This is represented in the formula by enclosing the NH_4^+ ion in parentheses with the subscript '$_2$' outside. The final empirical (simplest) formula is then written as $(NH_4)_2SO_4$.

Another example involves calcium nitrate, also a popular fertilizer source. From Table 1-3, the calcium ion is Ca^{+2} while the nitrate ion is NO_3^-. Again, the total positive and negative charge represented in the formula must be equal to zero. Because the positive charge is 2 (Ca^{+2}) and the negative charge is 1 (NO_3^-), two nitrate ions are needed to make the algebraic sum equal to zero. The formula is written as $Ca(NO_3)_2$.

Examples:

Assign oxidation numbers to each element in the following:

1. P_4 With any free element (those not bonded to any other element), the oxidation number of each atom is zero, therefore the oxidation number of P = 0.
2. H_2SO_4 Since the oxidation of H = $^+1$ and O = -2 and the sum of all elements in the formula must equal zero, this can be deduced by writing the oxidation number over each element and the total oxidation number for that element underneath it.

$$\text{oxidation number of each element} \rightarrow +1 \quad ? \quad -2$$
$$\text{formula} \rightarrow H_2 \quad S \quad O_4$$
$$\text{total oxidation number of each element} \rightarrow +2 \quad ? \quad -8 \; = 0$$

The oxidation number of H = $+1$; since two H^+ atoms are present, the total oxidation number of all H^+ is $+2$. Similarly, the total oxidation number of O is -8 ($-2 \times 4 = -8$). To determine the oxidation number of S, algebraically add the total values to equal zero:

$$+2 \text{ (from } H_2) + ? \text{ (S)} + -8 \text{ (from } O_4, 4 \times -2) = 0; \quad ? = +6$$

Since there is only one S atom, +6 is the oxidation number of S.

oxidation number of each element $\rightarrow$ +1   +6 -2

formula $\rightarrow$ H_2 S O_4

total oxidation number of each element $\rightarrow$ +2   +6 $-8 = 0$

3. $Au(NO_3)_3$ In this example, the oxidation number of Au and N are not known. However, from Table 1-3, it is seen that the total oxidation value of $NO_3 = -1$, therefore, the oxidation value of N can be found.

oxidation number of each element $\rightarrow$? -2

formula $\rightarrow$ N $O_3{}^{-1}$

total oxidation number of each element $\rightarrow$? -6 $= -1$

For N; $? + {}^{-}6 = -1$. Thus, the oxidation value of N must be +5. To determine the value of Au, set up the whole equation:

oxidation number of each element $\rightarrow$? -2 -2

formula $\rightarrow$ Au   (N $O_3)_3$

total oxidation number of each element $\rightarrow$?   +15 -18 $= 0$

For Au, ? = +3.

Naming Inorganic Compounds

Many rules and exceptions are involved when correctly naming inorganic compounds. These are listed and explained in Appendix B.

IONS AND IONIC INTERACTIONS

Chemical bonds are the forces holding atoms together in elements, compounds, and metals. When chemical reactions occur, chemical bonds break in the reactants and form in the products. The two major types of chemical bonds are **ionic bonds** and **covalent bonds,** which are formed by the transfer and sharing of valence (or oxidation) electrons, respectively. **Valence electrons** are the electrons in the outermost, or valence shell. All elements in a group usually have the same number of valence electron(s) in the valence shell. For example, the elements in Group 17 have seven valence electrons. Possession of the same number of valence electrons by all members of a group is the reason the members of a group have similar properties.

Atoms tend to stabilize or complete their valence shells and remain in a lower energy state. For many atoms, the simplest way to attain a completely filled outer energy level is to gain or lose one or more electrons. The following example

involves aluminum ionizing where Al^0 contains 3 electrons in its outer shell. To remain in its lower energy state, the Al^0 will lose the 3 valence electrons:

$$Al^0 + energy \rightarrow Al^{+++} + 3 \text{ electrons}$$

In another example, a chlorine atom (atomic number 17) needs one electron to complete its outer energy level which contains seven electrons; a sodium atom (atomic number 11) has a single electron in its outer level. If an atom of sodium approaches an atom of chlorine, there is a tendency for the outer electron of the sodium atom to be attracted and added to the outer shell of the chlorine atom which has the higher electronegativity. Each atom would then have a stable electron structure. This outer electron of sodium (Na) is strongly attracted by the chlorine atom (which is highly electronegative, Cl), and a transfer from the sodium atom to the chlorine atom occurs (Figure 1-6).

Although an atom such as sodium may have a strong tendency to lose an electron, electrons do not fly off into space; instead, they are transferred from one atom to another during a chemical reaction or are returned to the original atoms where the energy is lowered. As a result of the transfer, the sodium and chlorine atoms have outer energy levels that are completely filled. Each atom now has an unbalanced (or unequal) numbers of electrons and protons: the sodium ion has 11 protons and 10 electrons (an extra positive charge, designated as Na^+); the chlorine ion has 17 protons and 18 electrons (an extra negative charge, designated as Cl^-). Such interactions involving the mutual attraction of oppositely charged ions (positive and negative) are called **ionic interactions,** and form **ionic bonds.** An ionic bond is a chemical bond resulting from the mutual attraction of oppositely charged ions (e.g., Na^+Cl^-). Metals, with relatively low ionization energies, transfer electrons to nonmetals (with high electron affinities) to form positive and negative ions, respectively. Potassium (atomic number 19) also has a single electron in its outermost energy level and reacts with chlorine to form potassium chloride (K^+Cl^- or KCl).

The calcium ion (Ca^{+2}) is formed by the loss of two electrons; it can attract and hold two Cl^- ions, forming calcium chloride ($Ca^{+2}Cl_2^-$ or $CaCl_2$) (the subscript 2
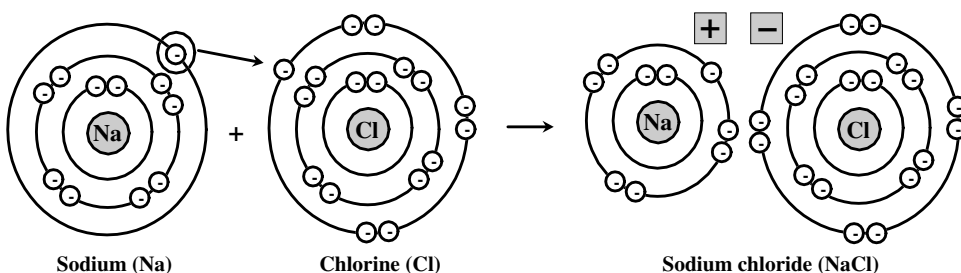
Figure 1-6. The formation of an ionic (attraction of opposite charges) bond where transferring a single unpaired valence electron gives sodium a stable arrangement (2 + 8) and gives chlorine the electron it needs to have all its energy levels full (2 + 8 + 8). Sodium attains a stable configuration by acting as an electron donor, passing a single outer shell electron to chlorine (an electron acceptor) in order to gain stability. In this process, sodium acquires a positive charge and chlorine a negative charge.

indicates that two atoms of chlorine are present for each atom of calcium). Similarly, magnesium has two valence electrons (two electrons in its outermost or valence shell); thus, one atom of magnesium can combine with two atoms of chlorine, giving up one electron from each to form magnesium chloride, $Mg^{+2}Cl_2^-$ or $MgCl_2$.
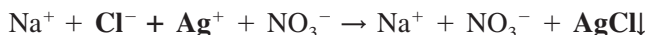
Small ions such as Na^+ and Cl^- make up less than 1% of the weight of most living matter, but they play crucial roles. For instance, Na^+ in minute quantities helps regulate stomatal opening and closing in plants but excessive amounts are often toxic. K^+ is the principal positively charged ion in many organisms, and many essential biological reactions occur only in its presence. Mg^{+2} is an integral part of chlorophyll, a molecule in green plants that traps light (radiant energy) from the sun and produces food in the form of glucose. Cl^- is also believed to be required for photosynthesis in chloroplasts.

When writing ionic equations for reactions in solution, strong electrolytes are indicated as being fully ionized, while nonelectrolytes and weak electrolyte formulas are written in the molecular form. Since insoluble substances and escaping gases do not ionize (form separated ions), they are also shown by molecular formulas.

1. Molecular form:

$$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl\downarrow$$

Ionic form:

$$Na^+ + \mathbf{Cl^-} + \mathbf{Ag^+} + NO_3^- \rightarrow Na^+ + NO_3^- + \mathbf{AgCl}\downarrow$$

2. Molecular form:

$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$$
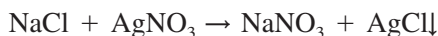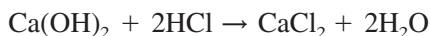
Ionic form: a neutralization reaction where water as a product is always shown in molecular form

$$Ca^{+2} + \mathbf{2OH^-} + \mathbf{2H^+} + 2Cl^- \rightarrow Ca^{+2} + 2Cl^- + \mathbf{2H_2O}$$

3. Molecular form:

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3\uparrow$$

Ionic form:

$$Na^+ + \mathbf{NO_3^-} + \mathbf{H^+} + HSO_4^- \rightarrow Na^+ + HSO_4^- + \mathbf{HNO_3}\uparrow$$
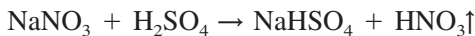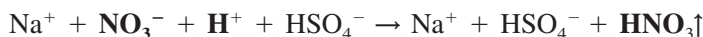
Molecules and Covalent Bonds

Another way for atoms to complete their outer energy levels (form chemical bonds) is by sharing electrons with other atoms that also seek an octet instead of being transferred between atoms as with ionic bonds. Chemical bonds formed by sharing
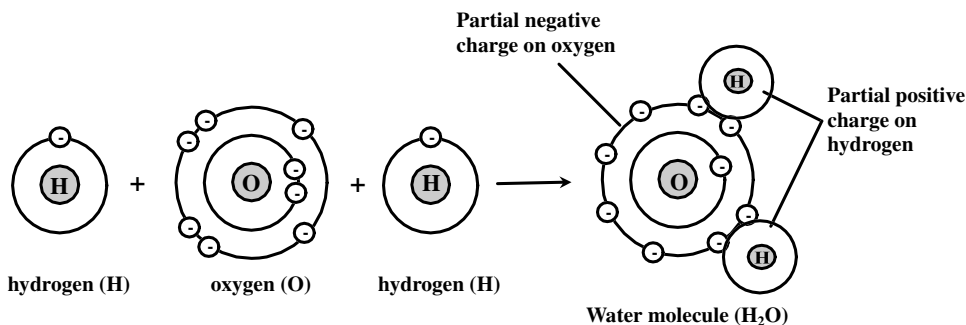
Figure 1-7. Covalent bonds from the mutual sharing of electrons between hydrogen (H) and oxygen (O) atoms to form water.

one or more pairs of electrons in overlapping orbitals are known as **covalent bonds.** With ionic bonds, an electron donor reacts electrically with an electron acceptor. With a covalent bond, each electron spends part of its time around one nucleus and part of its time around the other and they are treated as if they were in the valence shell of each atom. Thus, the sharing of electrons completes the outer energy level of each atom. For example, with water (H_2O), each hydrogen atom needs one more electron to complete its outer shell (Figure 1-7). Each oxygen atom has eight protons and eight electrons. Two of the electrons are in the first shell and six in the second shell, so oxygen needs two more electrons to stabilize its outer shell. If two hydrogen atoms share their electrons with one oxygen atom, the requirement of all three are satisfied and water is formed.

Another example is ammonia, NH_3, where its nitrogen atom has seven protons and has seven electrons, two in the inner shell and five in the outer shell (Table 1-1). Nitrogen needs three electrons to fill its outer shell to achieve an octet (eight); hence, it combines with three hydrogen atoms to form NH_3 which shares its three electrons with the three unpaired electrons of nitrogen.

Elements that form two-atom (or diatomic) molecules with a single covalent bond are H_2, F_2, Cl_2, Br_2, and I_2, O_2, and N_2.

Carbon-Atom Combinations. Of primary importance in living systems is the capacity of carbon to form covalent bonds. Carbon (atomic number 6) has four electrons in its outer energy level. It can share each of these four valence electrons with another carbon atom(s) or with other atoms, forming covalent bonds and producing a stable, filled outer energy level (8 electrons). In methane (CH_4), for example, one carbon atom shares one electron with each of four hydrogen atoms and in carbon dioxide (CO_2), four electrons are shared with each of two oxygen atoms (O::C::O or O=C=O), forming two double covalent bonds. Because carbon is neither strongly electropositive nor strongly electronegative, the covalent bonds formed may be with different elements, most often hydrogen (H), oxygen (O), phosphorus (P), sulfur (S), nitrogen (N), or with other carbon atoms. In fatty acids, the first carbon in the chain bonds with three hydrogen atoms and the next carbon atom. The next carbon atoms share two electrons with each of two hydrogen atoms and each of two more carbon atoms. A carboxyl group (–COOH) is attached to

the end of this chain. An example involves stearic acid, a 18-carbon containing fatty acid obtained from animal fat, designated as $C_{17}H_{35}COOH$ or $CH_3(CH_2)_{16}COOH$.

Stearic Acid
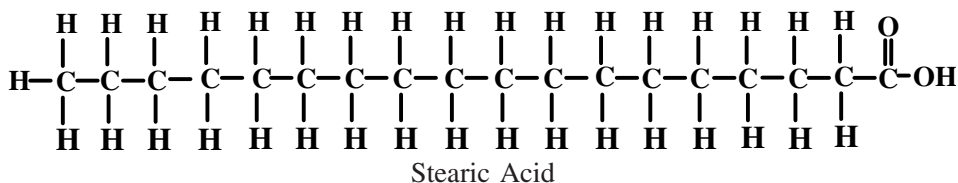
Because carbon reacts so readily with other carbon atoms, it can form long chains as well as more complex ring structures. This element can also form double and triple covalent bonds with another carbon atom(s).

Types of Covalent Bonds. Atoms can form three types of covalent bonds, single, double, and triple bonds, depending on how many other atoms it shares electrons with. There are various ways in which atoms can form covalent bonds and fill their outer energy levels. In the water molecule (H_2O) one of the oxygen electrons participates in a covalent bond with one hydrogen atom and the other in a covalent bond with a different hydrogen atom (remember that hydrogen atoms need only two electrons). Two **single bonds** are formed, and all three atoms have filled outer energy levels.
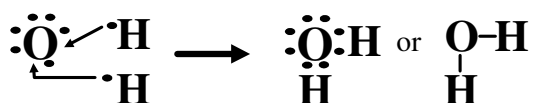
Note that oxygen has two unpaired electrons in its excited state, allowing it to form two bonds with hydrogen ions.

The bonding situation is different in another familiar substance, carbon dioxide (CO_2). In this molecule each oxygen atom is joined to the carbon atom by two pairs of electrons (four total electrons). Such bonds are called **double bonds** (e.g., O=C=O). Carbon atoms can form double bonds with each other as well as with other elements, as in ethylene, $H_2C=CH_2$, a fruit ripener and growth regulator, and the components of some fats and oils. Although somewhat rare, carbon atoms can also form **triple bonds** (in which three pairs of electrons are shared), such as with acetylene (HC≡CH), a fuel in welding and cutting of metals.

Single bonds are flexible, allowing the bonded atoms to rotate in relation to one another. Double bonds are much more rigid, restrict the relative movement of the bonded atoms, and have a higher bond energy than single bonds. Carbon-carbon triple bonds, however, tend not to be very stable as its electrons have a great deal of energy and are typically broken easily.

The nitrogen diatomic molecule (N_2) contains a triple bond that is extremely strong. Lightning with its tremendous energy passes though the atmosphere and will break these bonds as well as those of oxygen. The strong antiseptic smell

present after an electrical storm is due to the formation of ozone (O_3) and nitrogen/oxygen combinations. Nitrogen makes up 78% of the air and acts as a dilution agent for the more chemically active oxygen. Oxygen reacts with most substances causing oxidation (rusting) and supports combustion. Without the nitrogen dilution factor, an apparent increase in the oxygen concentration would increase the ease in which matter burns. The friction from walking might cause shoe soles to burn, while a golf ball rolling across a green might catch itself and the grass on fire.

Polar Covalent Bonds. As noted previously, elements differ in electronegativity (their attraction for electrons). In covalent bonds between atoms of different elements, the electrons are not shared equally between the two atoms. The shared electrons tend to spend more time around the nucleus of the more electronegative atom. As a consequence, this part of the molecule has a slightly negative charge, and the region around the less electronegative atom in the molecule has a slightly positive charge.

Covalent bonds in which electrons are shared unequally are known as **polar covalent bonds.** Such bonds often involve oxygen, which is highly electronegative. In molecules that are perfectly symmetrical, such as carbon dioxide, the unequal charges cancel out and the molecule as a whole is nonpolar. However, in asymmetrical molecules such as water, the molecule as a whole is polar, with regions of partial negative charge and regions of partial positive charge. Many of the special properties of water, upon which life depends, result largely from its polar nature.

Using the Lewis Dot system to construct molecules gives clues to the shape of a molecule and also helps to determine if the bond is polar or nonpolar.

In summary, ionic interactions, polar covalent bonds, and nonpolar covalent bonds may be considered as chemical bonds that differ widely in electronegativity between combining atoms. In ionic interactions, there is no electron sharing but rather an electrostatic attraction between oppositely charged ions (e.g., Na^+ and Cl^-). If the electronegativity between two elements is >1.6, the bond is ionic. In polar covalent bonds, electrons are shared, but, because of a difference in electronegativity between bonding atoms (e.g., H and O), they are shared unequally. The greater the electronegativity difference, the more polar the bond will be, as long as this difference is not greater than 1.6. In totally nonpolar covalent bonds, electrons are shared equally; such bonds exist only between identical atoms, as in H_2, Cl_2, O_2, and N_2.

Molecular and Structural Formulas

The properties of molecules depend on their three-dimensional structure—the shape and volume of space occupied by electrons in their outermost energy levels (orbitals). Chemists have developed methods for representing molecules on paper that allow them to keep track of all the atoms and bonds. *Molecular formulas indicate the number and types of atoms in a molecule; structural formulas show the way in which the atoms are bonded to one another.* Sometimes two or more compounds can have the same molecular formula but different structural formulas; such compounds are called **isomers.** Glucose and fructose are one such example, with both having a chemical formula of $C_6H_{12}O_6$ while having different structures.

Isomers
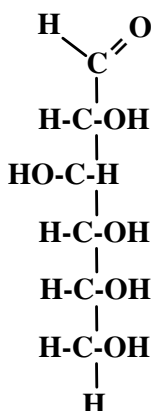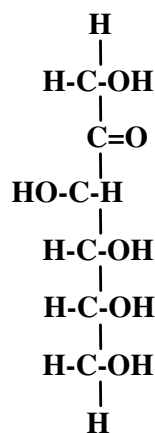
| Glucose Formula | Fructose Formula |

SOLUBILITY

Aqueous (water) solutions may contain a wide spectrum of substances. A **solution** (also called **a homogenous mixture**) is a uniform mixture of molecules or ions of two or more substances. The substance present in the largest amount, usually a liquid, is called the **solvent**; whereas, the substances present in lesser amounts are called **solutes.** For example, vinegar is a solution containing 3 to 5% acetic acid by weight and the rest is water (both are liquids): acetic acid is the solute and water is the solvent. In another example, salt is the solute in seawater (Table 1-4). The number of solute molecules in a given volume of solvent is the **solute concentration.** The terms *dilute* and *concentrated* refer to relatively low and high solution concentrations, respectively, but are indeed arbitrary.

The actual solubility of a substance depends on the nature of the solute, the nature of the solvent, temperature, pressure, and other factors which are sometimes difficult to predict. The dissolving of any solute in any solvent provides an illustration of equilibrium. When a solid is placed in water, solute particles immediately go into solution and may be dispersed throughout the solution. As the process continues, the concentration of solute in solution increases, and the rate at which

TABLE 1-4. Types of Solutions

Solute	Solvent	Example
Gas in a	Gas	Air
Gas in a	Liquid	Carbonated beverages [$CO_2(g)$ in $H_2O(l)$]
Gas in a	Solid	$H_2(g)$ in palladium (Pd(s))
Liquid in a	Liquid	Vinegar [$CH_3COOH(l)$ in $H_2O(l)$]
Liquid in a	Solid	Dental amalgam [Hg(l) in Ag(s)]
Solid in a	Liquid	Seawater [NaCl(s) in $H_2O(l)$]
Solid in a	Solid	Brass [Zn(s) in Cu(s)]

solute particles dissolve increases until a state of equilibrium is reached. Equilibrium occurs when the rate at which the solute particles are going into solution equals the rate at which they are returning to the solid state and the solution is then referred to as **saturated.**

Not all substances form true solutions in water. If clay is mixed with water, very little clay actually dissolves. Particles of clay are huge compared to molecules of water. The result is a muddy, heterogeneous mixture called a **suspension.** Some mixtures appear to be true solutions; however, upon close inspection small particles are revealed which seem permanently suspended. These particles are bombarded from all sides by water molecules (referred to as the **Brownian motion**), and this molecular action keeps them from settling out. Mixtures of this type are called **colloidal suspensions. Colloids** are substances that, when mixed with water, do not pass through semipermeable membranes. A simple way to distinguish between a true solution and a colloidal suspension involves passing a beam of light through each. A true solution is transparent, while the particles in a colloidal suspension appear cloudy or milky as the suspension disperses light much like dust particles in a beam of light or water particles in fog in a car headlight. This scattering of light by colloidal dispersions is called the **Tyndall effect.**

Types of Colloids. Various types of colloidal dispersions exist based on the physical states of the colloidal particles and of the homogenous mixture (Table 1-5). Water is the most important dispersion medium followed by air and other solvents and gases.

Emulsions are colloidal dispersions of liquid in liquid. Ordinarily, mixing two immiscible liquids will not produce a stable emulsion unless a third substance, called an *emulsifying agent,* is added. Kerosene and water, for example, normally do not mix but will if some soap or gelatin is also present. With pesticide formulations, *emulsifiable concentrates* are oily (or nonpolar) liquids that form emulsions (droplets of oil surrounded by water) in water (polar) instead of forming true solutions. The *emulsifying agent* acts as a binder-coupler between the oil-water surface, reducing interfacial tension and allowing the tiny droplets of oil to remain in suspension. This allows water-insoluble pesticides to be uniformly dispersed in water, even though each maintains its original identity. After emulsifiable concen-

TABLE 1-5. Colloidal Dispersions (Modified from Umland and Bellama, 1999)

Name	Colloidal Solute	Medium	Examples
Foam	Gas	Liquid	Whipped cream, shaving cream, suds
Foam	Gas	Solid	Foam rubber, marshmallows, sponge, Styrofoam, Ivory Soap, pumice
Aerosol	Liquid	Gas	Fog, clouds, aerosol sprays
Aerosol	Solid	Gas	Smoke, airborne viruses
Emulsion	Liquid	Liquid	Homogenized milk, mayonnaise
Emulsion	Liquid	Solid	Butter
Gel (sol)	Solid	Liquid	Gelatin (Jell-O), cream, milk of magnesia, mud, detergents, paints, toothpaste
—	Solid	Solid	Many alloys, ruby glass

trate compounds are added to water, the resulting emulsions are milky colored and require mild agitation to keep the pesticide uniformly suspended in the spray tank.

Soaps and detergents are colloidal particles made up of clusters of small particles. They clean by a colloidal phenomenon. Soaps consist of molecules with long hydrocarbon chains attached to negative (polar) groups. They form colloidal dispersions in water where the negative ends of the molecules are soluble in water and attract the positive ends of water molecules. The other end of the hydrocarbon chains are nonpolar and attach themselves to organic particles, such as grease droplets, in the water. This forms a roughly spherical **micelle** cluster around the grease particle, with the hydrocarbon chains extending inward and the negative ends at the outside of the sphere. The water then removes the organic particle from the soiled object and carries it away (refer to Figure 2-2).

Detergents and soaps are **surfactants** or *surface-active agents.* Surfactants concentrate at the surface of water and reduce surface tension (hydrogen bonding between water molecules) and expand the surface area. Thus, surfactants make water-wet surfaces better. Surfactants are used in many chemical solutions to increase the surface area covered by the spray solution (reduce surface tension). Soaps and detergents are discussed further in **Chapter Four.**

A true solution is formed when a solute, consisting of molecules or ions, is dispersed throughout the solvent to form a homogeneous mixture. A true solution exists in a *single phase.* The solute is said to be soluble in the solvent. A colloidal suspension, meanwhile, is a *two-phase system.* It has dispersed particles rather than a solute, and a dispersing medium rather than a solvent. The system consists of finely divided particles that remain suspended in the medium. Molecular motion (kinetic energy) of water molecules keeps particles dispersed for a period of time until gravity causes particles to settle because of their density.

Increasing the rate at which a solid dissolves in a liquid depends on the nature of the solid and liquid involved. In general, the rate of solution of a solid in a liquid can be increased by: (1) stirring to bring fresh portions of the solvent in contact with the undissolved solid; (2) grinding the solid into a powder which greatly increases the surface area being exposed to the liquid; and (3) heating the solvent to increase the kinetic activity of the solute particles. Stirring is a common means for turfgrass and agricultural managers to help suspend various materials in spray tanks. The stirring device, called an agitator, circulates water through the tank to help maintain a suspension, thus preventing settling of suspended particles.

For most solutes there is a limit to the concentration of solute molecules that a given solvent will accept at a given temperature. A solution is **saturated** when this limiting solute concentration is reached, and often excess solute molecules aggregate to form masses such as crystals. A solid that separates from a solution is called a **precipitate.** It may be possible to heat such solutions and allow more solute to dissolve. If all the solute dissolves and the solution then cools, recrystallization may not occur as the excess solute remains in solution. If this occurs, a **supersaturated** solution has formed. A supersaturated solution is so unstable that shaking a sprayer containing a supersaturated solution may produce enough shock to cause the excess solute to recrystallize, or adding more solute to this solution may cause recrystallization, leaving a saturated solution.

The formation of solutions usually increases the disorder (or entropy) of a system. In addition, energy changes always accompany the dissolving of a solute. It

is not easy to predict whether the overall solution process will be endo- or exothermic. Energy is always required to separate particles that are attracted to each other, and such forces of attraction exist in any solid. Temperature is a common factor that disturbs a system in equilibrium. Increasing the temperature of a saturated solution often dissolves more ions, affecting the solubilities of different compounds at various temperatures. The solubility of gases dissolved in liquids decreases as temperature increases. This is why bubbles of gas usually form inside a beaker of water as it is heated. Since the water was saturated with air at the lower temperature, and the solubility of the gas decreases as the temperature rises, some of the gas will leave the solution by forming bubbles, as the temperature rises.

Pressure also influences the amount of gas that dissolves in a given quantity of a liquid at a given temperature. *An increase in pressure increases the solubility of a gas.* This is known as **Henry's Law.** In a bottle of carbonated beverage, for example, a certain amount of carbon dioxide is dissolved at a given pressure. If the cap of the bottle is removed, the pressure above the contents immediately drops to atmospheric pressure. Since the solubility of CO_2 is lower at this lower atmospheric pressure, some of the gas in the solution escapes as bubbles and the solution becomes saturated with the gas at a lower concentration corresponding to the lower pressure. If the bottle remains open, CO_2 continues to diffuse into the surrounding air and is replaced by air. Eventually the pressure of CO_2 inside the bottle drops to the very lowest level of this gas naturally in the atmosphere (about 0.04%) and the beverage now tastes "flat," or "sweet."

Henry's Law

At a given temperature, the solubility of a gas is in direct proportion to the pressure above the solution:

$$Cg = kp_{gas}$$

where Cg is the concentration of the dissolved gas,
     k is the constant characteristic of the gas,
     p_{gas} is the pressure of the gas above the solution.

Solubility and Polarity. The nature of the solvent and solute are important in the solution process since a substance dissolves when its particles mix freely with those of the solvent. In general, polar molecules dissolve in polar solvents; nonpolar molecules dissolve in nonpolar solvents. In other words, "like dissolves like" is true. Not only does the solute weaken hydrogen bonds between water molecules but charged ions are attracted to the polar regions of the solvent. The electrostatic attractions of these polar ions are strong enough to separate the water molecules from one another, thus intermingling of the particles can occur and a solution results.

In nonpolar substances, such as fat and gasoline, the molecules are held by weak van der Waals (intermolecular) forces. These substances do not dissolve in water because their attractive forces are too weak to separate water molecules from one another. However, if nonpolar substances are mixed together the molecules are able

to intermingle freely to form a solution because they are attracted by similar weak forces, and are separated.

Alcohols have polar bonds at the hydroxyl end of the molecule and nonpolar bonds within the hydrocarbon end. They are able to dissolve both polar and nonpolar solvents. For example, the alcohol ethanol has the molecular formula of $CH_3—CH_2—OH$, with the OH being the polar end and the CH_3 having nonpolar bonds.

SOLUTION CONCENTRATIONS

A number of ways exist of quantitatively expressing the relative amounts of solute and solvent or of solute and solution. Solution concentrations may be expressed in terms of weight percentage, molarity, molality, parts per million, millimoles, and equivalents. Each method has advantages when used for specific purposes.

Molecular Weights and Concentrations

When dealing with a solution, the concentration depends upon the relative proportions of solute and solvent. The more solute dissolved in a solvent, the more concentrated the solution becomes. Meanwhile, the more solvent added, the more dilute the solution becomes. The weight of solute per 100 grams of solvent in this solution is known as its **solubility.** At a given temperature, the terms dilute and concentrated are qualitative and chemists have developed several methods for expressing solution concentrations quantitatively.

Molecules, as well as atoms, are measured in units called **moles.** A mole is a specific number of chemical particles. One mole of any substance contains the same number of particles (atoms, ions or molecules) as 1 mole of any other substance. This number, 6.022×10^{23}, is known as **Avogadro's number.** For example, 1 mole of sodium contains 6.022×10^{23} atoms of sodium; 1 mole of chloride ions contains 6.022×10^{23} Cl^- ions; and 1 mole of water contains 6.022×10^{23} molecules of water. One can think of moles in the same way as a pair or a dozen, since each represents a numerical quantity.

$$1 \text{ pair} = 2 \text{ objects}$$

$$1 \text{ dozen} = 12 \text{ objects}$$

$$1 \text{ mole} = 6.022 \times 10^{23} \text{ particles}$$

One mole of gold, for example, contains just as many atoms as one mole of lead, just as there are as many socks in a pair of socks as there are shoes in a pair of shoes. The **molecular weight** of a substance is the sum of the atomic weights of all the atoms in a molecule. For example, the molecular weight of carbon dioxide, CO_2, is the sum of the atomic weights of one carbon and 2 atoms of oxygen; $12 + 16 + 16$, or 44 g. For a brief review of the metric system, which is used exclusively in chemistry, refer to **Appendix C.**

One mole of a substance weighs an amount, in grams, that is numerically equal to its atomic weight (or molecular weight). For example, the molecular weight of

$CaCl_2$ is 111 g; therefore, 111 g of $CaCl_2$ is one mole (contains 6.022×10^{23} molecules) of $CaCl_2$. Also, one mole of sodium weighs 23 grams, and one mole of water (H_2O) weighs 18 grams. In another example, to obtain 5.0 moles of oxygen (O_2) molecules, 5.0×32 g $= 160$ g of oxygen must be measured. To obtain 5.0 moles of hydrogen (H_2) molecules, 5.0×2.0 g $= 10$ g of hydrogen must be present. These two quantities, 160 g of oxygen and 10 g of hydrogen, contain the same number (6.02×10^{23}) of molecules.

The mole is useful for defining quantities involved in chemical reactions. In order to form water, for example, 2 moles of hydrogen atoms and 1 mole of oxygen atoms combine to produce 1 mole of water molecules as shown: $2H_2 + O_2 \rightarrow 2H_2O$. Similarly, to make table salt (NaCl), 1 mole of sodium (about 23 grams) would combine with 1 mole of chlorine (about 35.5 grams) to form 1 mole of NaCl which weighs 58.5 g as shown: $2Na + Cl_2 \rightarrow 2NaCl$.

In another example, one mole of carbon atoms (12 g of C) reacts completely with one mole of oxygen molecules (32 g of O_2) to form carbon dioxide in the reaction: $C + O_2 \rightarrow CO_2$, because one mole of carbon and one mole of molecular oxygen contain exactly the same number of carbon atoms and oxygen molecules.

Determining Empirical Formulas. The empirical formula for a compound consists of the symbols of the constituent elements in their smallest whole-number ratio (e.g., H_2O or NaCl). The first step in determining the empirical formula of a compound is to convert the gram ratio of each element to a mole ratio. The mole ratio is then adjusted to its simplest whole-number ratio.

Example: What is the empirical formula of a compound containing 75 g C and 25 g H?

Step 1: convert gram ratio of each element to mole ratio

for $\qquad$ C: 75 g C $\times \dfrac{1 \text{ mole C}}{12 \text{ g C}} = 6.25$ moles C

for $\qquad$ H: 25 g H $\times \dfrac{1 \text{ mole H}}{1 \text{ g H}} = 25$ moles H

Step 2: adjust mole ratio to a simplest whole-number ratio by dividing the mole ratios by the smaller value. If a whole number does not appear, it is necessary to multiply each number in the ratio by a value that will create the simplest whole number ratio.

$$C = \frac{6.25}{6.25} = 1 \qquad H = \frac{25}{6.25} = 4$$

Therefore, the empirical formula is C_1H_4 or CH_4, which is a gas, methane. To successfully understand and work with various units (e.g., weights and volumes) within chemistry, refer to Appendix D on Unit Analysis.

Example Problems:

1. What is the simplest formula of a compound containing 20 g Ca, 6 g C, and 24 g O_2? The molecular weights of Ca = 40 g, C = 12 g, and O = 16 g. Ca = 20 g/40 g = 0.5 mole; C = 6 g/12 g = 0.5 mole; O = 24 g/16 g = 1.5 mole, therefore, $Ca_{0.5}C_{0.5}O_{1.5}$ or $CaCO_3$.
2. What is the weight (or mass), in grams (g), of 3.50 moles of copper atoms? First, determine the atomic weight of copper which is 63.5 g, then insert the following:

$$3.50 \text{ moles} \times \frac{63.5 \text{ g Cu}}{\text{mole}} = 222 \text{ g Cu}$$

3. What percentage of nitrogen (N) and potassium (K) are in the fertilizer, potassium nitrate, KNO_3?

   Step 1: determine the molecular weight of each element in KNO_3

$$K = 1 \times 39 = 39 \text{ g}$$
$$N = 1 \times 14 = 14 \text{ g}$$
$$O_3 = 3 \times 16 = \underline{48 \text{ g}}$$
$$\text{total } 101 \text{ g}$$

   Step 2: Now determine the percentage of each element in KNO_3 by dividing the total weight of each element by the total formula weight of the compound. To express the value as a percent, multiply the results by 100.

$$K = \frac{39 \text{ g}}{101 \text{ g}} = 0.386 \text{ or } 38.6\%$$

$$N = \frac{14 \text{ g}}{101 \text{ g}} = 0.139 \text{ or } 13.9\%$$

$$O_3 = \frac{48 \text{ g}}{101 \text{ g}} = 0.475 \text{ or } 47.5\%$$

   Therefore, pure KNO_3 contains 38% K, 14% N, and 48% O. To check the results, add up the percentage of each element in the formula. This should equal 100 (38 + 14 + 48 = 100).
4. (a) How many moles of atoms are in 6.20 g of phosphorus? The atomic weight of P is 31 g, thus,

$$6.20 \text{ g P} \times \frac{1 \text{ mole}}{31 \text{ g P}} = 0.20 \text{ mole}$$

   (b) How many moles are contained in 900 g of glucose, $C_6H_{12}O_6$?

Step 1: Determine the molecular weight of glucose.

$$C_6 \ (6 \times 12 \ g) + H_{12} \ (12 \times 1 \ g) + O_6 \ (6 \times 16 \ g) = 180 \ g$$

Step 2: Calculate the number of moles in 900 g.

$$\text{moles} = 900 \ g \times \frac{1 \ \text{mole}}{180 \ g} = 5.0 \ \text{moles of } C_6H_{12}O_6$$

5. (a) How many moles of oxygen are in 8.0 g of O_2?

$$8.0 \ g \ O_2 \times \frac{1 \ \text{mole}}{32 \ g \ O_2} = 0.25 \ \text{moles } O_2$$

(b) How many molecules of O_2 are in 8.0 g of O_2 gas?

$$0.25 \ \text{mole } O_2 \times \frac{6.02 \times 10^{23} \ \text{molecules}}{1 \ \text{mole } O_2} = 1.5 \times 10^{23} \ \text{molecules } O_2$$

6. What is the empirical formula of a compound containing 92.3% C and 7.7% H? C = 12 g/m; H = 1 g/m.

Step 1: calculate the number of moles in each element.

$$\text{Moles of carbon atoms} = \frac{92.3 \ g}{12 \ g/m} = 7.7 \ \text{moles}$$

$$\text{Moles of hydrogen atoms} = \frac{7.7 \ g}{1 \ g/m} = 7.7 \ \text{moles}$$

Step 2: determine the mole ratio of each element in the compound.

Mole ratio for carbon: $\dfrac{7.7}{7.7} = 1.0$

Mole ratio for hydrogen: $\dfrac{7.7}{7.7} = 1.0$

Therefore, the simplest formula is C_1H_1 or CH.

7. Determine the simplest formula for a compound with hydrogen = 2.04%, sulfur = 32.65%, and oxygen = 65.31%.

atom	percent of compound	÷	atomic weight	=	relative no. of atoms	÷	least common denominator	=	whole no. ratios
H	2.04	÷	1	=	2.04	÷	1.02	=	2
S	32.65	÷	32	=	1.02	÷	1.02	=	1
O	65.31	÷	16	=	4.08	÷	1.02	=	4

Therefore, the simplest formula is H_2SO_4.

8. Determine the weight of the following.
   (a) 1.0 mole of $Na_2S_2O_3$

$$Na = 2 \times 23.0 = 46.0 \text{ g}$$
$$S = 2 \times 32.0 = 64.0 \text{ g}$$
$$O = 3 \times 16.0 = \underline{48.0 \text{ g}}$$
$$\text{total } 158 \text{ g/m}$$

(b) 0.50 mole of CO_2

$$0.50 \text{ mole} \times \frac{[12 + 2(16) \text{ g}]}{\text{mole}} = 22 \text{ g}$$

(c) 1.0×10^{-3} mole of $C_{254}H_{377}N_{65}O_{75}S_6$

$$C = 254 \times \quad 12 = 3048$$
$$H = 377 \times \quad 1.0 = 377$$
$$N = \quad 65 \times 14.0 = 910$$
$$O = \quad 75 \times 16.0 = 1200$$
$$S = \quad 6 \times \quad 32 = \underline{192}$$
$$\text{total } 5727 \text{ (or } 5.73 \times 10^3) \text{ g/mole}$$

$$1.0 \times 10^{-3} \text{ mole} \times \frac{5.73 \times 10^3 \text{ g}}{\text{mole}} = 5.73 \text{ g}$$

(d) 3.60 mole of $Pb(NO_3)_2$

$$3.60 \text{ mole} \times \frac{[207 + 2(14) + 6(16) \text{ g}]}{\text{mole}} = 1.19 \times 10^3 \text{ g}$$

9. How many moles of phosphoric acid (H_3PO_4) are needed to neutralize 0.9 mole of sodium hydroxide (NaOH)? $H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + H_2O$ a 3 to 1 ratio exists between NaOH and H_3PO_4; therefore,

$$0.9 \text{ mole NaOH} \times \frac{1 \text{ mole } H_3PO_4}{3 \text{ mole NaOH}} = 0.3 \text{ mole } H_3PO_4$$

Calculations Based on Chemical Reactions

A chemical formula indicates the number and kind of atoms that make up a molecule of a compound. Since each atom is an entity with a characteristic mass, a formula also provides a means for computing the relative weights of each kind of

atom in a compound. In a balanced chemical equation, the coefficients show the relative number of moles of each substance involved. The combined weight of the reaction products is exactly equal to the combined weight of the original reactants. The ability to balance and interpret equations should enable calculations involving the relative masses of substances involved in chemical reactions, if we understand mole, mass, and volume relationships. These are known as **stoichiometric calculations.** For the following reaction:

$$A \rightarrow B$$

$$\text{mass of } A \times \frac{1 \text{ mol } A}{\text{gfm } A} \rightarrow \text{mol } A \times \frac{b \text{ mol } B}{a \text{ mol } A} \rightarrow \text{mol } B \times \frac{\text{gfm } B}{1 \text{ mol } B} \rightarrow \text{mass of } B$$

Mass-mole conversion   Mole ratio from   Mole-mass conversion
                               balanced equation

A = given quantity of a reactant or product,
B = wanted quantity of a reactant or product,
a = number of moles of G in the balanced chemical equation,
b = number of moles of W in the balanced chemical equation,
gfm = gram-formula mass.

For the reaction of hydrogen and oxygen to form water, the equation may be read as 2 moles of hydrogen react with 1 mole of oxygen to form 2 moles of water. Also, since the weights of a mole of hydrogen and of oxygen can be readily determined from the atomic weights, the weight relationship between reactants and products can be calculated:

$$2H_2 \quad + \quad O_2 \quad \rightarrow \quad 2H_2O$$
$$\text{2 moles} \quad \text{1 mole} \quad \text{2 moles}$$
$$\text{4 g} \quad \text{32 g} \quad \text{36 g}$$
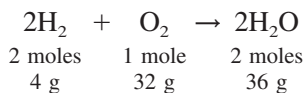
The equation describes the ratios of moles that react when different amounts of substances are involved. If 65 moles of oxygen are available, then:

$$130 \text{ moles } H_2 + 65 \text{ moles } O_2 \rightarrow 130 \text{ moles } H_2O$$

Steps for solving limited (stoichiometric) chemical reactions include:

1. Write a balanced equation for the reaction (if it is not given).
   (a) Write what is given and what is asked for.
   (b) Write the formula masses needed.
2. If quantities of more than one reactant are given, determine which reactant is limiting. The quantity of the limiting reactant determines the amount of product formed and the amounts of other reactants that react.
3. Set up and perform the calculation(s):
   (a) Use formula masses to convert grams of the given quantity to moles by using the numerical value of the formula mass.

(b) Use the equation for the reaction to write conversion factors for converting moles of one substance to moles of other substances.

(c) Use formula masses to convert moles to grams. Be sure to include formulas of substances in labels.

Example:

Show the calculations on how many grams of oxygen are needed to produce 36 g of water from the following reaction:
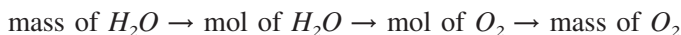
$$2H_2 \ + \ O_2 \ \rightarrow \ 2H_2O$$

$$\begin{array}{ccc} ?\ g & ?\ g & 36\ g \\ 2\ \text{moles} & 1\ \text{mole} & 2\ \text{moles} \end{array}$$
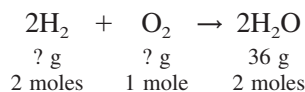
A = given quantity of a reactant or product,   = H_2O
B = wanted quantity of a reactant or product,   = O_2
a = number of moles of A in the balanced chemical equation, = 2
b = number of moles of B in the balanced chemical equation. = 1

The basic steps in the calculations are:

mass of $H_2O \rightarrow$ mol of $H_2O \rightarrow$ mol of $O_2 \rightarrow$ mass of O_2

$$\text{Mass of } A \times \frac{1 \text{ mol } A}{\text{gfm } A} = \text{mol } A$$

or

$$36 \text{ g } H_2O \times \frac{1 \text{mol } H_2O}{18 \text{ g } H_2O} = \frac{2 \text{ mol}}{H_2O}$$

$$\text{mol } A \times \frac{b \text{ mol } B}{a \text{ mol } A} = \text{mol } B$$

or

$$\frac{2 \text{ mol}}{H_2O} \times \frac{1 \text{ mol } O_2}{2 \text{ mol } H_2O} = \frac{1 \text{ mol}}{O_2}$$

$$\text{mol } B \times \frac{\text{gfm } B}{1 \text{ mol } B} = \text{mass of } B$$

or

$$\frac{1 \text{ mol}}{O_2} \times \frac{32 \text{ g } O_2}{1 \text{ mol } O_2} = 32 \text{ g } O_2$$

gfm = gram-formula mass.

Table 1-6 can be used to solve any stoichiometry problem. In short, this table represents that in order to find the mass of a reactant or product, the number of moles in the balanced chemical equation must be determined as shown above:

TABLE 1-6. Relationship Between Mass, Mole, and Volume in Chemical Reactions

$$\text{Mass of } A \times \frac{1 \text{ mol } A}{\text{gfm } A} \rightarrow \text{mol } A \times \frac{b \text{ mol } B}{a \text{ mol } A} \rightarrow \text{mol } B \times \frac{\text{gfm}}{1 \text{ mol } B} \rightarrow \text{mass of } B$$

$$\text{Representative particles of } A \times \frac{1 \text{ mol } A}{6.02 \times 10^{23}} \rightarrow \text{mol } A \times \frac{b \text{ mol } B}{a \text{ mol } A} \rightarrow \text{mol } B \times \frac{6.02 \times 10^{23}}{1 \text{ mol } B} \rightarrow \text{Representative particles of } B$$

$$\text{Volume of } A \text{ (L) at STP} \times \frac{1 \text{ mol } A}{22.4 \text{ L } A} \rightarrow \text{mol } A \times \frac{b \text{ mol } B}{a \text{ mol } A} \rightarrow \text{mol } B \times \frac{22.4 \text{ L } B}{1 \text{ mol } B} \rightarrow \text{volume of } B \text{ (L) at STP}$$

A = given quantity of a reactant or product,
B = wanted quantity of a reactant or product,
a = number of moles of G in the balanced chemical equation,
b = number of moles of W in the balanced chemical equation,
gfm = gram-formula mass.

Example:

1. (a) How many moles of carbon dioxide are produced by burning 1.50 moles ethyl alcohol (C_2H_5OH) in the following reaction?

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$
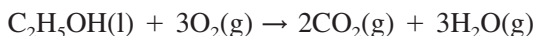
From the equation, the mole relationship between C_2H_5OH and CO_2 is obtained to form a conversion factor:

$$\frac{2 \text{ moles } CO_2}{1 \text{ mole } C_2H_5OH}$$

Multiplying the mole ratio (conversion factor) by the given number of moles of C_2H_5OH yields:

$$1.5 \text{ moles } C_2H_5OH \times \frac{2 \text{ moles } CO_2}{1 \text{ mole } C_2H_5OH} = 3.00 \text{ moles } CO_2$$

(b) Now determine how many grams of CO_2 are produced when 1.50 moles of C_2H_5OH is burned.

Multiply 3.00 moles of CO_2 by a factor that changes moles CO_2 into grams of CO_2. The factor is the gram-molecular mass in units of g/mole derived from the formula CO_2 and the atomic masses of carbon and oxygen.

$$1.50 \text{ moles } C_2H_5OH \times \frac{2.00 \text{ moles } CO_2}{\text{mole } C_2H_5OH} \times \frac{44.0 \text{ g } CO_2}{\text{mole } CO_2} = 132 \text{ g } CO_2$$

(c) How many grams of CO_2 are produced when 23 g C_2H_5OH is burned?

Three steps are needed to determine this:

(1) Convert grams C_2H_5OH into moles C_2H_5OH:

$$23 \text{ g } C_2H_5OH \times \frac{\text{mole } C_2H_5OH}{46 \text{ g } C_2H_5OH} = 0.50 \text{ moles } C_2H_5OH$$

(2) Convert moles C_2H_5OH into moles CO_2:

$$0.50 \text{ moles } C_2H_5OH \times \frac{2.00 \text{ moles } CO_2}{\text{mole } C_2H_5OH} = 1.0 \text{ moles } CO_2$$

(3) Convert moles CO_2 into grams of CO_2:

$$1.0 \text{ moles } CO_2 \times \frac{44 \text{ g } CO_2}{\text{mole } CO_2} = 44 \text{ g } CO_2$$

The complete step for these three conversions is:

$$23 \text{ g } C_2H_5OH \times \frac{\text{mole } C_2H_5OH}{46 \text{ g } C_2H_5OH} \times \frac{2.00 \text{ moles } CO_2}{\text{mole } C_2H_5OH} \times \frac{44 \text{ g } CO_2}{\text{mole } CO_2} = 44 \text{ g } CO_2$$

(d) How many grams of CO_2 are formed when 32 g O_2 reacts with 23 g C_2H_5OH?

This reaction involves determining the amount of the reactants that may be in excess and not completely consumed. The amount of product is determined by the reactant that is not in excess. A preliminary calculation is needed to determine which reactant is in excess.

(1) Calculate the moles of each reactant:

For oxygen:

$$32 \text{ g } O_2 \times \frac{\text{mole } O_2}{32 \text{ g } O_2} = 1.0 \text{ mole } O_2$$

For ethyl alcohol:

$$23 \text{ g } C_2H_5OH \times \frac{\text{mole } C_2H_5OH}{46 \text{ g } C_2H_5OH} = 0.5 \text{ mole } C_2H_5OH$$

It is not apparent which is in excess; therefore, calculate the moles of one reactant needed to react with the given quantity of the second reactant:

(2) Calculate the moles of O_2 required to react with 0.50 mole C_2H_5OH.

$$0.5 \text{ mole } C_2H_5OH \times \frac{3 \text{ mole } O_2}{\text{mole } C_2H_5OH} = 1.5 \text{ mole } O_2$$

Since 1.5 moles of O_2 are required and only 1.0 mole is available, the ethyl alcohol must be in excess and the amount of CO_2 produced will be determined by the O_2 present.

(3) Calculate the moles and grams of CO_2 produced:

$$1.0 \text{ mole } O_2 \times \frac{2.0 \text{ moles } CO_2}{3 \text{ moles } O_2} = 0.66 \text{ moles } CO_2 \text{ produced}$$

$$0.66 \text{ moles } CO_2 \text{ produced} \times \frac{44.0 \text{ g } CO_2}{\text{mole } CO_2} = 29 \text{ g } CO_2$$

(e) How many liters of CO_2 are produced at STP when 23.0 g ethyl alcohol is burned?

The first step is to convert 44.0 g CO_2 into moles and then convert moles into liters at standard conditions, temperature/pressure (abbreviated, STP). The conversion factor for this is 22.4 L/mole, which is the volume of 1 mole of any gas at STP.

(1) Convert gram CO_2 to mole CO_2:

$$44.0 \text{ g } CO_2 \times \frac{1 \text{ mole } CO_2}{44.0 \text{ g } CO_2} = 1.00 \text{ mole } CO_2$$

(2) Convert mole CO_2 to volume (in liters) CO_2 using the 22.4 L/mole conversion:

$$1.00 \text{ mole } CO_2 \times \frac{22.4 \text{ L } CO_2}{\text{mole } CO_2} = 22.4 \text{ L } CO_2$$

The complete step is:

$$23 \text{ g } C_2H_5OH \times \frac{\text{mole } C_2H_5OH}{46 \text{ g } C_2H_5OH} \times \frac{2.00 \text{ moles } CO_2}{\text{mole } C_2H_5OH} \times \frac{22.4 \text{ L } CO_2}{\text{mole } CO_2} = 22.4 \text{ L } CO_2$$

2. From the Haber process, ammonia is formed by reacting hydrogen with nitrogen under heat and pressure as shown:

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

(a) How many grams of H_2 are needed to react with 168 g of N_2?
(b) How many grams of NH_3 can be produced?

Step 1: below each symbol, write what is given and what must be found:

$$3H_2 + N_2 \rightarrow 2NH_3$$
$$\text{?g} \quad\quad 168 \text{ g} \quad\quad \text{?g}$$
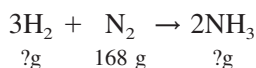
Step 2: change the grams of given N_2 into moles:

$$\text{moles } N_2 = (168 \text{ g}) \times \frac{1 \text{ mole}}{28 \text{ g}} = 6 \text{ moles}$$

Step 3: using the coefficients of the balanced equation, obtain moles of H_2 needed and NH_3 produced:

$$\text{moles H}_2 = (6 \text{ moles N}_2) \times \frac{3 \text{ moles H}_2}{1 \text{ mole N}_2} = 18 \text{ moles}$$

$$\text{moles NH}_3 = (6 \text{ moles N}_2) \times \frac{2 \text{ moles NH}_3}{1 \text{ mole N}_2} = 12 \text{ moles}$$

Step 4: calculate the grams of H_2 needed and NH_3 produced:

$$\text{g H}_2 = (18 \text{ moles}) \times \frac{2 \text{ g}}{1 \text{ mole}} = 36 \text{ g}$$

$$\text{g NH}_3 = (12 \text{ moles}) \times \frac{17 \text{ g}}{1 \text{ mole}} = 204 \text{ g}$$

Therefore, 36 g of H_2 plus 168 g N_2 equal the grams (204 g) of NH_3. This can be summarized as:

$$\text{mass N}_2 \times \frac{\text{mol N}_2}{\text{gfm N}_2} \times \text{mol N}_2 \times \frac{b \text{ mol NH}_3}{a \text{ mol N}_2} \times \text{mol NH}_3 \times \frac{\text{gfm NH}_3}{\text{mol NH}_3} = \text{mass NH}_3$$

$$168 \text{ g N}_2 \times \frac{\text{mol N}_2}{28 \text{ g N}_2} = 6 \text{ mol N}_2$$

$$6 \text{ mol N}_2 \times \frac{2 \text{ mol NH}_3}{1 \text{ mol N}_2} = 12 \text{ mol NH}_3$$

$$12 \text{ mol NH}_3 \times \frac{17 \text{ g NH}_3}{\text{mol NH}_3} = 204 \text{ g NH}_3$$

3. (a) Calculate the weight of iron when 16 g FeO_2 reacts with CO. (b) What weight of CO is required for the reaction? (c) What weight of CO_2 is formed?

$$\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$$

1 mole	3 mole	2 mole	3 mole
16 g	? g	? g	? g
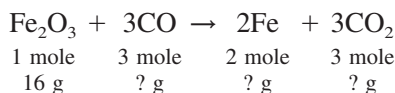
(a) $16 \text{ g Fe}_2\text{O}_3 \times \dfrac{\text{mol Fe}_2\text{O}_3}{160 \text{ g Fe}_2\text{O}_3} = 0.10 \text{ mol Fe}_2\text{O}_3$

$$0.10 \text{ mol Fe}_2\text{O}_3 \times \frac{2 \text{ mol Fe}}{\text{mol Fe}_2\text{O}_3} = 0.20 \text{ mol Fe}$$

$$0.20 \text{ mol Fe} \times \frac{55.8 \text{ g Fe}}{\text{mol Fe}} = 11.2 \text{ g Fe}$$

(b) $0.10 \text{ mol } Fe_2O_3 \times \dfrac{3 \text{ mol } CO}{\text{mol } Fe_2O_3} = 0.30 \text{ mol } CO$

$$0.30 \text{ mol } CO \times \dfrac{28 \text{ g } CO}{\text{mol } CO} = 8.4 \text{ g } CO$$

(c) $0.10 \text{ mol } Fe_2O_3 \times \dfrac{3 \text{ mol } CO_2}{\text{mol } Fe_2O_3} = 0.30 \text{ mol } CO_2$

$$0.30 \text{ mol } CO_2 \times \dfrac{44 \text{ g } CO_2}{\text{mol } CO_2} = 13.2 \text{ g } CO_2$$
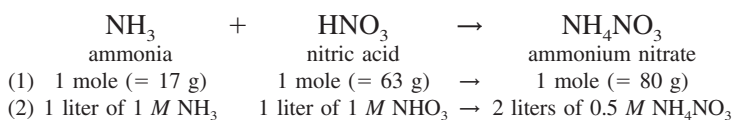
Molarity

For counting chemical particles by measuring volumes of solutions, concentrations of a compound and its components are commonly expressed as molarity. **Molarity** (designated as M) is the number of moles of a compound dissolved in 1 liter of solution.

$$\text{Molarity, } M = \frac{\text{moles of solute}}{\text{liter of solution}}$$

A *molar solution* contains 1 mole of solute (or 6.022×10^{23} molecular of a subtance) in one liter of solution. For example, 1 liter of a 1 molar (1 M) solution of glucose ($C_6H_{12}O_6$) is prepared by adding water to 1 mole of glucose (molecular weight: 180 g) until the volume of the solution reaches 1 liter. Half this quantity of glucose (90 g) in 1 liter of solution forms a 0.5 M solution. Twice this quantity (360 g) per liter of solution yields a 2 M solution. Two moles of solute is formed from each of the following: adding 1 M solute concentration in 2 liters or adding 2 M solute in 1 liter or adding 4 M solute in 0.5 liter.

Name	Symbol	Solute Unit	Solution Unit	Dimensions	
Molarity	M	mole	liter solution	$\dfrac{\text{mole solute}}{\text{liter solution}} =$	$\dfrac{\frac{\text{g of solute}}{\text{g/mole}}}{\text{liters of solution}}$

The number of moles of reagent in a solution equals the product of the molarity (M) of a solution and the volume (V) of that solution: $M \times V =$ moles. For example, (1) the following will yield exactly 1 mole of ammonium nitrate (NH_4NO_3), while (2) accounts for a volume of a specific molarity.

$$NH_3 \quad + \quad HNO_3 \quad \rightarrow \quad NH_4NO_3$$
ammonia   nitric acid   ammonium nitrate
(1)   1 mole (= 17 g)   1 mole (= 63 g)   →   1 mole (= 80 g)
(2) 1 liter of 1 M NH$_3$ 1 liter of 1 M NHO$_3$ → 2 liters of 0.5 M NH$_4$NO$_3$

Example:

1. How many moles of household ammonia (NH_3) are in 1.2 liters of a solution that is 0.50 M ammonia?

   By using the definition of molarity as the number of moles of solute per liter of solution:

   $$1.2 \text{ liter} \times \frac{0.5 \text{ moles } NH_3}{\text{liter}} = 0.60 \text{ moles } NH_3$$

2. What volume of the 0.5 M ammonia solution is needed to obtain 1.8 M of ammonia?

   Now the number of moles needed is divided by the molarity:

   $$1.8 \, M \, NH_3 \times \frac{\text{liters}}{0.5 \, M \, NH_3} = 3.6 \text{ liters}$$

3. If the solution runs out in Example 2, what weight of ammonia is needed to prepare an additional 5 liters of 0.50 M ammonia?

   Step 1: First convert between moles of ammonia and grams of ammonia using its molecular weight:

   $$
   \begin{array}{lll}
   \text{N:} & 1 \times 14 \text{ g} = & 14 \text{ g} \\
   \text{H:} & 3 \times 1 \text{ g} = & \dfrac{3 \text{ g}}{17 \text{ g}}
   \end{array}
   $$

   Step 2: Now determine the total grams of ammonia needed in 5 liters to obtain a 0.5 M solution.

   $$5 \text{ liters} \times \frac{0.5 \, M}{\text{liter}} \times \frac{17 \text{ g } NH_3}{M} = 42 \text{ g } NH_3$$

   The desired solution contains 42 g of ammonia in 5 liters of solution.

4. A bottle of concentrated ammonia contains 28.0% (by mass) NH_3 and has a density of 0.898 g/mL. What is the molarity of the NH_3?

   Step 1: Determine how many moles of ammonia are in 1.0 L by using the density to find the mass of 1 L of concentrated ammonia.

   $$\frac{0.898 \text{ g}}{mL} \times \frac{1000 \text{ mL}}{\text{liter}} = \frac{898 \text{ g solution}}{\text{liter solution}}$$

   Step 2: The solution only contains 28.0% (by mass) NH_3; thus, find out how many grams of ammonia are in 1 liter.

$$\frac{898 \text{ g}}{\text{liter}} \times \frac{28.0 \text{ g NH}_3}{100 \text{ g}} \times \frac{251 \text{ g NH}_3}{\text{liter}}$$

Step 3: Now convert grams NH_3 to moles NH_3 (the molecular weight of NH_3 is 17 g).

$$\frac{251 \text{ g NH}_3}{\text{liter}} \times \frac{1 \text{ mole NH}_3}{17 \text{ g NH}_3} = \frac{14.8 \text{ mole NH}_3}{\text{liter}} \quad \text{or} \quad 14.8 \text{ } M \text{ NH}_3$$

With practice, these steps can be combined as:

$$\frac{0.898 \text{ g}}{\text{mL}} \times \frac{1000 \text{ mL}}{\text{liter}} \times \frac{28.0 \text{ g NH}_3}{100 \text{ g}} \times \frac{1 \text{ mole NH}_3}{17 \text{ g NH}_3} = \frac{14.8 \text{ mole NH}_3}{\text{liter}} \quad \text{or } 14.8 \text{ } M \text{ NH}_3$$

Examples:

1. What weight of calcium bromide ($CaBr_2$) is needed to prepare 150 mL of a 3.50 M solution?

$$\frac{\text{mole solute}}{\text{liter solution}} = \frac{\dfrac{\text{g solute}}{\text{g/mole}}}{\text{liters solution}}$$

$$3.50 \text{ } M = \frac{\dfrac{\text{g CaBr}_2}{200 \text{ g CaBr}_2/\text{mole}}}{150 \text{ mL} \times 1 \text{ liter}/1,000 \text{ mL}}$$

This can be rearranged as follows:

$$\text{g CaBr}_2 = \frac{3.50 \text{ moles}}{\text{liter}} \times 150 \text{ mL} \times \frac{1 \text{ liter}}{1,000 \text{ mL}} \times \frac{200 \text{ g}}{\text{mole}}$$

$$= 105 \text{ g CaBr}_2$$

2. What is the molarity of a solution containing 17.1 g of granulated sugar ($C_{12}H_{22}O_{11}$) dissolved in 0.5 liter of solution? (The molecular weight of sugar is 342 g.)

Step 1: the moles of solute and liters of solution need to be calculated.

$$\text{moles solute:} \quad 17.1 \text{ g sugar} \times \frac{\text{mole sugar}}{342 \text{ g sugar}} \times 0.0500 \text{ moles sugar}$$

Step 2: calculate molarity as mole solute per liter of solution.

$$\text{molarity:} \quad \frac{\text{mole solute}}{\text{liter solution}} = \frac{0.0500 \text{ moles sugar}}{0.500 \text{ liters solution}} = \frac{0.100 \text{ moles}}{\text{liter}} = 0.100 \text{ } M$$

3. How many grams of sucrose ($C_{12}H_{22}O_{11}$) are in 1 liter of 0.25 M solution?

   $C_{12}H_{22}O_{11}$ = 342 g/m and 0.25 M = 0.25 m/L; therefore,
   1 liter contains 342 g/m × 0.25 m/L = 86 g.

4. What is the molarity of a solution of KCl in water if 74 g are dissolved per liter of solution?

   KCl = 39 + 35 g/m = 74 g/m; therefore,
   74 g/L = 1.0 M solution

5. (a) Find the molarity, weight per liter solution, and weight per liter of 88% by weight and 1.802 g/mL density H_2SO_4 (sulfuric acid), (1 mole H_2SO_4 = 98.1 g).

   The density of a solution is a function of the concentration of solute and is commonly shown on a bottle label.

   $$\text{weight of 1 liter} = \frac{1.802 \text{ g solution}}{\text{mL}} \times \frac{1,000 \text{ mL}}{\text{liter}}$$

   $$= 1,802 \text{ g/liter}$$

   $$\text{weight } H_2SO_4 \text{ per liter} = \frac{1,802 \text{ g solution}}{\text{liter}} \times \frac{88 \text{ g } H_2SO_4}{100 \text{ g solution}}$$

   $$= 1,586 \text{ g } H_2SO_4/\text{liter}$$

   $$\text{molarity} = \frac{\text{mole solute}}{\text{liter solution}} = \frac{\dfrac{\text{g solute}}{\text{g/mole}}}{\text{liters solution}}$$

   $$= \frac{1,586 \text{ g } H_2SO_4/\text{liter}}{98.1 \text{ g } H_2SO_4/\text{mole}} = 16.2 \text{ mole } H_2SO_4/\text{liter}$$

   (b) What volume of 16.2 M H_2SO_4 solution is needed to prepare 3 L of 6 M solution?

   $$\text{moles } H_2SO_4 \text{ needed} = V \times M = 3 \text{ liters} \times \frac{6 \text{ moles } H_2SO_4}{\text{liter}} = 18 \text{ moles}$$

   $$\text{volume of 16.2 } M \text{ solution needed} = \frac{18 \text{ moles } H_2SO_4}{16.2 \text{ moles } H_2SO_4/\text{liter}} = 1.11 \text{ liter}$$

6. A label of the herbicide Roundup Pro indicates 41% by weight of the active chemical glyphosate, as an isopropylamine salt, is present. Convert this to grams per liter and pounds active ingredient glyphosate per gallon of solution. Average density is 1.18 gmL, and molecular weight of glyphosate ($C_6H_{17}N_2O_5P$) is 228.19 g.

$$\frac{1.18 \text{ g}}{\text{mL}} \times \frac{1000 \text{ mL}}{\text{liter}} \times \frac{41 \text{ g } C_6H_{17}N_2O_5P}{100 \text{ g}} = \frac{480 \text{ g } C_6H_{17}N_2O_5P}{\text{liter}}$$

to convert to pounds active ingredient (designated as "ai") per gallon:

$$\frac{480 \text{ g}}{\text{liter}} \times \frac{1 \text{ lb}}{454 \text{ g}} \times \frac{3.785 \text{ liter}}{\text{gal}} = \frac{4 \text{ lbs ai}}{\text{gal}}$$

7. What mass of silver nitrate ($AgNO_3$), expressed in grams, is needed to prepare 0.500 liter of a 0.100 M solution?

   Step 1: calculate the moles of solute needed:

   $$\text{moles solute} = \frac{0.100 \text{ moles}}{\text{liter}} \times 0.500 \text{ liter} = 0.0500 \text{ moles}$$

   Step 2: calculate the grams of solute needed:

   $$0.05 \text{ moles } AgNO_3 \times \frac{170 \text{ g } AgNO_3}{\text{mole } AgNO_3} = 8.50 \text{ g } AgNO_3$$

   One step could be used to solve this problems where:

   $$\frac{0.1 \text{ moles } AgNO_3}{\text{liter}} \times 0.500 \text{ liter} \times \frac{170 \text{ g } AgNO_3}{\text{mole } AgNO_3} = 8.50 \text{ g } AgNO_3$$

8. How many grams of HCl are dissolved in 200 mL of a 0.3 M HCl solution?

   $$200 \text{ mL} \times \frac{1 \text{ L}}{1,000 \text{ mL}} = 0.2 \text{ L; therefore,}$$

   $$\frac{0.3 \text{ moles HCl}}{\text{liter}} \times 0.2 \text{ liter} \times \frac{35.5 \text{ g HCl}}{\text{mole HCl}} = 2.2 \text{ g HCl}$$

9. How would one prepare 2 liters of a 3.5 M H_2SO_4 solution?

   $$3.5 \text{ } M \text{ } H_2SO_4 = \frac{3.5 \text{ mole}}{\text{liter}} \times \frac{98 \text{ g}}{\text{mole}} = 343 \text{ g/L; therefore,}$$

   dissolve 646 g H_2SO_4 with enough water to make 2 liters of total solution.

Parts per Million

Another means of expressing exceedingly small concentrations is parts per million (ppm). One expression of ppm is the concentration of one milligram (mg) of one substance distributed through one kilogram (kg) of another. For example, the concentration of potassium iodide, KI, in iodized table salt is about 7.6×10^{-5} g of KI per gram of NaCl. This can be converted into ppm by the following: a million

$\times$ 1,000,000 = 10^6. Since the concentration of KI in table salt is 7.6×10^{-5} g KI per gram NaCl and we want to know how many grams of KI are in 10^6 g of table salt, multiply both the numerator and denominator by 1,000,000:

$$\frac{7.6 \times 10^{-5} \text{ g KI}}{1 \text{ g NaCl}} \times \frac{10^6}{10^6} \times \frac{7.6 \times 10 \text{ g KI}}{10^6 \text{ g NaCl}} = 7.6 \times 10 \text{ ppm KI} = 76 \text{ ppm KI}$$

ppm also represents the concentration of one milligram of one substance dissolved throughout one liter of another (usually water).

Examples:

1. What is the concentration of Cu^{+2} ions, in parts per million, of a 750 mL aqueous solution containing 14.38 mg of Cu^{+2} ions (parts per million = mg/L)?

$$750 \text{ mL} \times \frac{1 \text{ L}}{1,000 \text{ mL}} = 0.7500 \text{ L, and,}$$

ppm is normally expressed as mg/L; therefore,

$$\frac{14.38 \text{ mg Cu}^{+2}}{0.750 \text{ L}} = 19.2 \text{ ppm Cu}^{+2}$$

2. What is the concentration, in ppm, of a 0.20% volume solution of isopropyl alcohol in water?

$$\text{ppm (vol)} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 10^6$$

$$= \frac{0.2 \text{ mL isopropyl alcohol}}{100 \text{ mL solution}} \times 10^6$$

$$= 2.0 \times 10^3 \text{ (or 2,000) ppm}$$

3. What is the Mn^{+7} concentration, in ppm, of a 3×10^{-7} *M* solution of manganese(VII)? ppm is expressed as mg/L, but the problem lists mole/L; therefore, this must be converted:

$$\frac{3 \times 10^{-7} \text{ mole Mn}^{+7}}{\text{L solution}} \times \frac{54.94 \text{ g Mn}^{+7}}{1 \text{ mole Mn}^{+7}} \times \frac{1,000 \text{ mg}}{1 \text{ g}}$$

$$= \frac{0.0164 \text{ mg Mn}^{+7}}{\text{L solution}} \text{ or 0.02 ppm Mn}^{+7}$$

Millimoles

In many measurements, especially with those dealing with soil, it is convenient to express the volume of a solution in milliliters instead of liters. Since a 1 *M* solution

contains one mole of solute per liter of solution, a milliliter of solution contains one-thousandth (1/1,000) of a mole or a millimole (m mol). This is a formula weight of solute expressed in milligrams; therefore,

$$\text{molarity of solution} = \frac{\text{m mol solute}}{\text{mL solution}} \quad \text{and}$$

$$\text{number of m mol of solute} = M \times V \text{ (or volume, mL)}$$

Thus, the weight of solute is: $\text{mg solute} = M \times V \text{ (mL)} \times \dfrac{\text{mg}}{\text{m mol}}$

If a measurement involves milliliters, it is often convenient to use m mol, mg, and mL.

Equivalent Weights

Solution concentration can be expressed to allow chemically equivalent quantities of different solutes to be measured simply. **Equivalent weights,** as the name implies, are the amounts of reactants that are equivalent (have the same combining capacity) to each other in chemical reactions. Two methods are used to determine equivalences. The first is the equivalent weight of an acid, which is that weight of the substance that furnishes 1 mole of hydronium (H_3O^+ or hydrogen, H^+) ions, while that of a base is the weight that furnishes 1 mole of hydroxide (OH^-) ions. The equivalent weight of an acid or a base is its molecular weight divided by the number of "equivalents" the compound supplies per mole—that is, the number of moles of hydronium (H_3O^+ or H^+) ions or OH^- ions available. For example, sulfuric acid, H_2SO_4, contains two equivalents of hydronium (H_3O^+ or H^+) ions based on its formula, while sodium hydroxide, NaOH, supplies one equivalent of hydroxide (OH^-) ions.

$$H_2SO_4 \text{ (aq)} \rightarrow 2H^+ \text{ (aq)} + SO_4^{-2} \text{ (aq)}$$

$$NaOH \text{ (aq)} \rightarrow Na^+ \text{ (aq)} + OH^- \text{ (aq)}$$
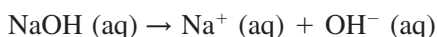
Thus, the equivalent weight of H_2SO_4 is 98/2 = 49 g, the equivalent weight of NaOH is 40/1 = 40 g, and the equivalent weight of H_3PO_4 is 98/3 = 32.7 g. For complete neutralization, 1 equivalent of a monoprotic (one H^+) acid is the same as 1 mole of the acid; 1 equivalent of a diprotic (2 H^+) acid is the same as one-half mole of the acid; and 1 equivalent of a triprotic (3H^+) acid is the same as one-third mole of the acid. Phosphoric acid (H_3PO_4), for example, is triprotic and can furnish 3 moles of H^+ ions per mole of acid, and its equivalent weight is one-third mole.

equivalent weight

$$= \frac{\text{molecular weight}}{\text{number of } H^+ \text{ or } OH^- \text{ per molecule}} \quad \text{or} \quad \frac{\text{molecular weight}}{\text{oxidation number (or valence)}}$$

From the equation $Zn + 2HCl \rightarrow ZnCl_2 + H_2$, one atomic weight of zinc reacts with two formula weights of HCl and replaces two atomic weights of hydrogen. To replace one equivalent weight of hydrogen, only one-half an atomic weight of zinc is needed. In the case of zinc, the equivalent weight is $65.4/2 = 32.7$.

The second measure of equivalents is the *chemical equivalents* of elements. This is the quantity, in grams, that supplies or acquires 1 mole of electrons in a chemical reaction. For example, a mole of sodium atoms (23 g) loses 1 mole of electrons to form 1 mole of Na^+ ions, while a mole of calcium atoms (40 g) supplies 2 moles of electrons when Ca^{+2} ions are formed and a mole of aluminum atoms (27 g) supplies 3 moles of electrons when Al^{+3} ions are formed. Thus, 1 equivalent of calcium is the mass of one-half mole of calcium atoms, 20 g (40 g ÷ 2), and 1 equivalent of aluminum is the mass of one-third mole of aluminum atoms, 9.0 g (27 g ÷ 3). The mass of 1 mole of atoms of the elements is divided by the change in oxidation state these atoms undergo in a chemical reaction. These relationships can be summarized as follows:

$$1 \text{ equivalent } Na^+ = \frac{1 \text{ mole Na}}{1 \text{ mole electron}} \times \frac{23 \text{ g Na}}{\text{mole Na}} = \frac{23 \text{ g Na}}{\text{mole electron (or equivalent)}}$$

$$1 \text{ equivalent } Ca^{+2} = \frac{1 \text{ mole Ca}}{2 \text{ moles electrons}} \times \frac{40 \text{ g Ca}}{\text{mole Ca}} = \frac{20 \text{ g Ca}}{\text{mole electron}}$$

$$1 \text{ equivalent } Al^{+3} = \frac{1 \text{ mole Al}}{3 \text{ moles electrons}} \times \frac{27 \text{ g Al}}{\text{mole Al}} = \frac{9.0 \text{ g Al}}{\text{mole electron}}$$

$$1 \text{ equivalent } Fe^{+3} = \frac{1 \text{ mole Fe}}{3 \text{ moles electrons}} \times \frac{55.8 \text{ g Fe}}{\text{mole Fe}} = \frac{18.6 \text{ g Fe}}{\text{mole electron}}$$

$$1 \text{ equivalent } Fe^{+2} = \frac{1 \text{ mole Fe}}{2 \text{ moles electrons}} \times \frac{55.8 \text{ g Fe}}{\text{mole Fe}} = \frac{27.9 \text{ g Fe}}{\text{mole electron}}$$

Examples of equivalent weights of some common acids and bases are listed in Table 1-7.

TABLE 1-7. Examples of Equivalent Weights of Some Acids and Bases

Substance	Formula	Molecular Weight	Equivalent Weight
Hydrochloric acid	HCl	36.5	36.5
Sulfuric acid	H_2SO_4	98.1	49.05
Phosphoric acid	H_3PO_4	98.0	32.7
Sodium hydroxide	NaOH	40.0	40.0
Calcium hydroxide	$Ca(OH)_2$	74.1	37.5

Examples:

1. How many equivalents are in 16 g of H_3PO_4? $H_3PO_4 \rightarrow PO_4^{-3} + 3H^+$

   Step 1: Determine the gram molecular weight of H_3PO_4: = 98.0 g

   Step 2: set up the equation to determine equivalent:

$$16.0 \text{ g } H_3PO_4 \times \frac{1 \text{ mole } H_3PO_4}{98.0 \text{ g } H_3PO_4} \times \frac{3 \text{ equiv } H_3PO_4}{1 \text{ mole } H_3PO_4} = 0.490 \text{ equivalence } H_3PO_4$$

2. Suppose one wished to neutralize 100 negative charges (CEC, $cmol_c/kg$) in a soil sample using the least amount of material. The cations at your disposal include H^+, K^+, Na^+, Ca^{+2}, Mg^{+2}, and Al^{+3}. Which cation would provide the least weight needed to neutralize these 100 grams of negative charges and which one would require the most weight to neutralize this?

   Step 1: the equivalent weight of each cation first needs to be determined which will satisfy the charges of one negative charge:

$$\text{equivalent weight (g)} = \frac{\text{molecular weight (g)}}{\text{oxidation number (or valence)}}$$

$$1 \text{ eq } H^+ = \frac{1 \text{ g}}{1} = 1 \text{ g } H^+ \qquad 1 \text{ eq } Na^+ = \frac{23 \text{ g}}{1} = 23 \text{ g } Na^+$$

$$1 \text{ eq } K^+ = \frac{39 \text{ g}}{1} = 39 \text{ g } K^+ \qquad 1 \text{ eq } Ca^{+2} = \frac{40 \text{ g}}{2} = 20 \text{ g } Ca^{+2}$$

$$1 \text{ eq } Mg^{+2} = \frac{24 \text{ g}}{2} = 12 \text{ g } Mg^{+2} \qquad 1 \text{ eq } Al^{+3} = \frac{27 \text{ g}}{3} = 9 \text{ g } Al^{+3}$$

   Since:

$$1 \text{ eq } H^+ = 1 \text{ eq } K^+ = 1 \text{ eq } Na^+ = 1 \text{ eq } Ca^{+2} = 1 \text{ eq } Mg^{+2} = 1 \text{ eq } Al^{+3}$$

   On an equivalent basis:

$$1 \text{ g } H^+ = 39 \text{ g } K^+ = 23 \text{ g } Na^+ = 20 \text{ g } Ca^{+2} = 12 \text{ g } Mg^{+2} = 9 \text{ g } Al^{+3}$$

   Step 2: Since 100 grams of negative charges need to be neutralized, these values are multiplied by 100. Therefore, 100 g H^+, 3,900 g K^+, 2,300 g Na^+, 2,000 g Ca^{+2}, 1,200 g Mg^{+2}, and 900 g Al^{+3} are needed to satisfy 100 negative charges. Hydrogen would require the least equivalent weight (100 g) to satisfy the 100 negative charges, while potassium would require the most (3,900 g).

Milliequivalent Weight. In biological sciences the term **milliequivalent** is often used when describing nutrients and their levels in soils. A milliequivalent (meq) is

that amount of an ion that will displace (or combine with) 1 milligram (mg) of hydronium (H_3O^+) (or hydrogen, H^+) ion. One mg is 1/1,000 of a gram. In soil science, a milliequivalent is the amount of a cation (positive ion) that will displace 1 mg of hydrogen ions from the active soil solids, which are clay and humus. That amount, expressed in mg, is called the milliequivalent weight (meq-weight). Thus, one meq-weight is that amount (in mg) of a cation that will displace 1 meq-weight (1 mg) of H^+. When dealing with meq, 1 equivalent equals 1,000 meq and 1 equivalent/1,000 equals 1 meq.

Example problem:

What is 1 milliequivalent (meq) of calcium (Ca^{+2})?

Step 1: the equivalence of calcium is determined:

$$1 \text{ equivalent } Ca^{+2} = \frac{40 \text{ g (atomic weight of Ca)}}{2 \text{ (valence charge of } Ca^{+2})} = 20 \text{ grams}$$

Step 2: this has to be converted to meq: therefore if 1 equivalent Ca^{+2} = 20 grams, then this is divided by 1,000 to obtain meq. Thus 1 meq of Ca^{+2} = 0.020 g = 20 mg. This can be rewritten as:

$$20 \text{ g } Ca^{+2} \times \frac{1 \text{ eq}}{1,000 \text{ meq}} \times \frac{1,000 \text{ mg}}{1 \text{ g}} = 20 \text{ mg}$$

CHEMICAL REACTIONS

When two substances capable of reacting with each other are mixed, their atoms, molecules, or ions, being in constant motion, begin to collide with one another. Those that collide with sufficient energy will react and form new substances. **Chemical reactions** involve the exchange of electrons between atoms. This often involves the breaking of bonds and the formation of new bonds. Reactions may be described by **chemical equations.** The participant(s) to the left of the arrow are the starting substances called **reactant(s)**; those to the right are the new substance(s) called **product(s)** formed in the reaction. For example, the balanced equation for the formation of water from oxygen gas and hydrogen gas is:

$$2H_2 + O_2 \rightarrow 2H_2O$$
$$\underbrace{\qquad}_{\text{— reactants —}} \quad \underbrace{\qquad}_{\text{product}}$$
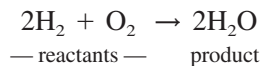
The arrow ($\rightarrow$) in the equation means ''forms'' and indicates the direction of the chemical change. The number and kind of atoms on the side of the product must equal the number and kind of atoms on the reactant side. The equation above tells us that two moles (molecules) of diatomic hydrogen (H_2) react with one mole (molecule) of diatomic oxygen(O_2) to yield two moles (molecules) of water. Another example involves preparing oxygen by heating mercury(II) oxide. Under the action of heat, mercury(II) oxide is decomposed into its two elements, mercury

(Hg) and oxygen (O_2). This reaction is represented by the following chemical equation:
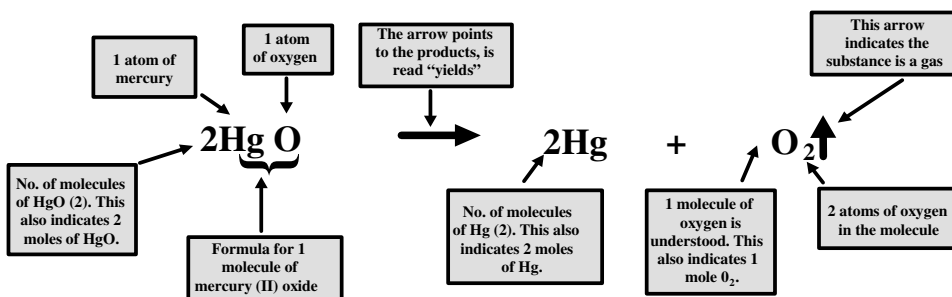
Whole number coefficients, such as two moles of water, are used in the above equation to comply with the *Law of Conservation of Atoms (or Mass).* This law states that the total number of each atom (or mass) involved in a chemical reaction remains constant. In other words, no new atoms are added or lost. A new species of atom cannot be represented on the product side and no species of atom can disappear from the reactant side. Balancing requirements are met by adjusting the coefficient in front of the reactants and products to the smallest possible whole numbers, ensuring the equation meets the requirements of the law of conservation of atoms. The letters 's,' 'l,' 'g,' and 'aq' are used to indicate where a substance is a solid (s), liquid (l), gas (g), or an aqueous (aq) or water solution.

$$2Na(s) \ + \ 2H_2O(l) \rightarrow \ 2NaOH(aq) \ + \ H_2(g)$$

sodium metal   water   sodium hydroxide   hydrogen gas
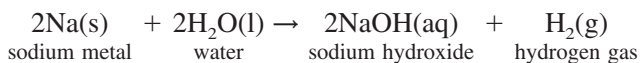
Balancing Chemical Reactions

To write an equation, the nature of the reactant(s) and product(s) must be known. Usually it is easier to find the composition of and identify the reactants. Balancing chemical equations is necessary to account for all molecules, atoms and/or ions and to ensure the law of conservation of atoms is met, where the total number of atoms on the reactant side of an equation must equal those found on the product side. *The total mass of the products must equal the total mass of the reactants.* Coefficients, therefore, are placed in front of the formulas to bring all elements into balance. However, since the formulas are fixed, balancing cannot be attempted by changing any of the subscripts in the formula. The following equation is not balanced since the total number of oxygen atoms on the left side of the equation does not equal those on the right side.

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

water   diatomic   diatomic
hydrogen   oxygen
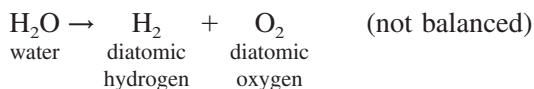
How can this equation be balanced? Many equations can be balanced by trial and error. A subscript '$_2$' may not be added to the oxygen (O) of the water molecule (H_2O) since this subscript would change the formula. Coefficients, therefore, are

used to balance the total number of each atom in an equation, not subscripts. The first step is to begin with the compound with the most atoms or most kinds of atoms and use one of those atoms as a starting point. Currently, two hydrogen (H) atoms are on each side of the reaction and are balanced; however, only one oxygen atom is on the left side and two oxygen atoms are on the right. If the number of water molecules is increased to 2 to indicate two moles combine:

$$2H_2O \rightarrow H_2 + O_2 \qquad \text{(not balanced)}$$

The second step is to balance elements appearing only once on each side of the reaction first. The equation is still not balanced since there are four hydrogen atoms on the left side of the equation but only two hydrogen atoms on the right. To balance the number of hydrogen atoms on the product side, a coefficient of 2 is placed in front of the hydrogen molecule, making it $2H_2$, as shown:

$$2H_2O \rightarrow 2H_2 + O_2 \qquad \text{(balanced)}$$

The equation is now balanced since the same number of each atom is found on both sides of the equation. In this case, the same number of hydrogen atoms (4) are on each side of the reaction as are oxygen molecules (2). When dealing with more complicated reactions, balance free elements such as O and H atoms last.

When a whole number coefficient is placed in front of a compound it applies to all atoms in that compound. For example: $2H_2O = 4$ atoms of H and 2 atoms of O. Similarly, when placed in front of a diatomic molecule, the product of the coefficient and subscript indicates the total number of atoms. The coefficients in an equation are always expressed to the smallest (simplest) whole number ratio. For example:

$$4H_2O \rightarrow 4H_2 + 2O_2 \text{ should be simplified to}$$

$$2H_2O \rightarrow 2H_2 + O_2$$
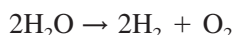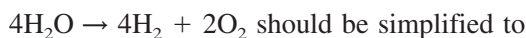
Summary of Steps for Writing Chemical Equations (Umland and Bellama, 1999).

1. Write a word equation after identifying the reactants and products.
2. Write symbols for elements (formulas for elements existing as polyatomic molecules) and correct formulas for compounds.
3. Balance by changing coefficients in front of symbols and formulas. Do not change formulas or add or remove substances (remember the Law of Conservation of Atoms, or Mass).
4. Check to see if the same number of each kind of atom is shown on both sides. If coefficients have a common divisor, simplify.
5. Add symbols showing whether substances are solids (s), liquids (l), gases (g), or in aqueous solution (aq). If the conditions required for the reaction to take place, such as catalysts, is known, write them over the arrow.
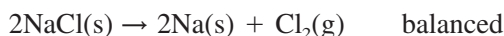
*Example:*

Balance the following word equation:

$$\text{sodium chloride (s)} \rightarrow \text{sodium metal (s)} + \text{chlorine gas (g)}$$

Step 1: Write the formulas for the reactants and products:

$$NaCl(s) \rightarrow Na\ (s) + Cl_2\ (g)$$

Step 2: Change coefficients in front of symbols and formulas. There is one chlorine atom on the left side of the equation but two on the right side. These are balanced by placing a 2 in front of the NaCl. To balance the sodium ions, a 2 is also placed in front of the Na.

$$2NaCl(s) \rightarrow 2Na(s) + Cl_2(g) \qquad \text{balanced}$$

Step 3: Subscripts cannot be changed to balance a chemical reaction. For example, the sodium chloride equation cannot be balanced by:

$$NaCl_2(s) \rightarrow Na(s) + Cl_2(g) \qquad \text{balanced, but wrong}$$
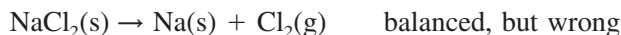
Coefficients must be placed in front of the symbol, not as subscripts, as $NaCl_2$ above is the incorrect formula for sodium chloride.

Types of Chemical Reactions

Four common types of reactions typically occur (Table 1-8).

Chemical Equilibrium

Most chemical reactions are reversible. When net change of the chemical concentration ceases, the reaction is said to be at equilibrium. Consider the following imaginary reaction:

$$A + B \rightleftharpoons C + D$$
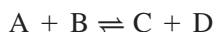
Equilibrium is reached when as many molecules of C and D are being converted to molecules of A and B as molecules of A and B are being converted to molecules of C and D. At equilibrium, the concentration of reactants does not have to equal the concentration of products. Only the *rates* of the forward and reverse reactions must be the same.

Suppose the reaction is set up so that only A and B molecules are present initially. At first, the reaction goes to the right, with A reacting with B to yield C and D. As C and D accumulate, the rate of the reverse reactions increases. At the same time, the rate of the forward reaction decreases because the concentrations of A and B are decreasing. At some point, the rates of the forward and reverse reactions equalize and no further changes in concentration take place. The propor-

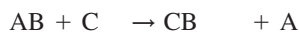**TABLE 1-8. Four Basic Types of Chemical Reactions**

1. **Combination (also called direct union composition or synthesis):** two or more substances combine to form (or synthesize) a more complex substance.
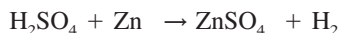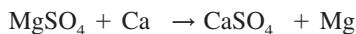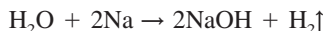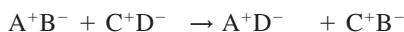
$$A + B \rightarrow AB$$

examples:

$$C + O_2 \rightarrow CO_2$$

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

$$SO_3 + H_2O \rightarrow H_2SO_4$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$
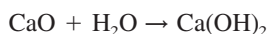
2. **Single replacement:** one substance is replaced in its compound by another substance, setting the replaced element free.

$$AB + C \rightarrow CB + A$$

examples:

$$H_2O + 2Na \rightarrow 2NaOH + H_2\uparrow$$

$$MgSO_4 + Ca \rightarrow CaSO_4 + Mg$$

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

3. **Double replacement (or ion exchange):** two substances replace (or exchange) their ions with two other substances.

$$A^+B^- + C^+D^- \rightarrow A^+D^- + C^+B^-$$

examples:

$$NaCl + AgNO_3 \rightarrow NaNO_3 + AgCl\downarrow \text{ (precipitant)}$$

$$2NaCl + H_2SO_4 \rightarrow Na_2SO_4 + HCl\uparrow \text{ (gas)}$$

$$NaCl + KNO_3 \rightleftharpoons NaNO_3 + KCl$$
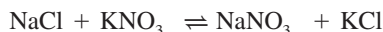
4. **Decomposition (or analysis):** one substance breaks down to form two or more simpler substances. This is a reversal of the composition reaction. Decomposition reactions are usually endothermic, requiring energy in the form of heat or electricity.
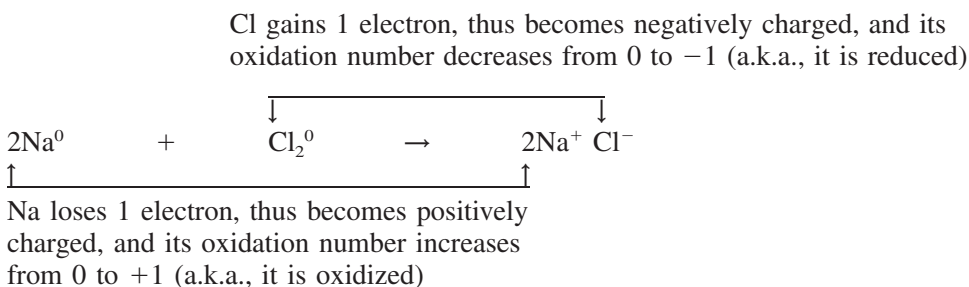
$$AB \rightarrow A + B$$

examples:

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

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

$$CaCO_3 \rightarrow CaO + CO_2$$

$$H_2CO_3 \rightarrow H_2O + CO_2$$

$$2KClO_3 \rightarrow 2KCl + 3O_2$$
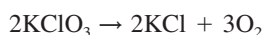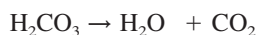
tions of reactants (A + B) and products (C + D) will remain the same. Increasing either the concentration or the temperature increases the rate of reaction. Catalysts can also speed up a reaction by bringing the particles close together on the catalyst surface.
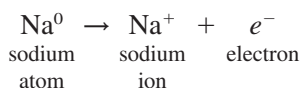
Oxidation-Reduction Reactions

Chemical reactions are essentially energy transformations in which stored energy in chemical bonds are transferred to other, newly formed chemical bonds. In such transfers, electrons shift from one energy level to another and in many reactions, electrons pass from one atom or molecule to another. An oxidation-reduction (also called redox) reaction is one in which electrons are transferred from one group or molecule to another. The charge that a molecule acquires is called its oxidation number or status. A simple reaction involving oxygen (or the oxidation of) in the presence of other elements forms *oxides* which are simple compounds of oxygen plus another element. A positive ion forms when a neutral atom is oxidized, while a negative ion forms when it is reduced. The original meaning of the term *oxidation* was the *addition of oxygen* to a compound, with the compound *losing the oxygen* being *reduced* (oxygen means ''acid former''). Today, oxidation, in a chemical context, refers to the loss of electrons (to become more positive; the oxidation number of an element increases), with the molecule or atom which *gains* those electrons (to become more negative; the oxidation number of an element decreases) being reduced. The total oxidation number of all atoms in a formula is always zero. The loss of the electron through loss of a hydrogen atom will accomplish the same purpose; thus if a molecule loses a hydrogen it will be oxidized, if it gains a hydrogen, it is reduced. Oxidation and reduction reactions always occur simultaneously. In the formation of common table salt (NaCl) the equation is written:

Cl gains 1 electron, thus becomes negatively charged, and its oxidation number decreases from 0 to -1 (a.k.a., it is reduced)

$$2Na^0 \quad + \quad Cl_2{}^0 \quad \rightarrow \quad 2Na^+ \ Cl^-$$

Na loses 1 electron, thus becomes positively charged, and its oxidation number increases from 0 to $+1$ (a.k.a., it is oxidized)

In this equation, both reactants are initially neutral (e.g., $2Na^0$, Cl^0). During the reaction, sodium loses an electron (becomes positively charged) and so is oxidized, while chorine gains that electron and becomes negatively charged and reduced. The oxidation of one substance in a reaction causes the reduction of another, and the number of electrons lost by one equals the number gained by the other. The number of electrons lost by the reducing agent must equal the number of electrons gained by the oxidizing agent. The only way to know if a reaction is redox or not is by assigning oxidation numbers to each element and observing if a change in oxidation number occurs for these elements. When viewed separately, each sodium atom loses an electron and is said to be oxidized and becomes a sodium ion. The oxidation
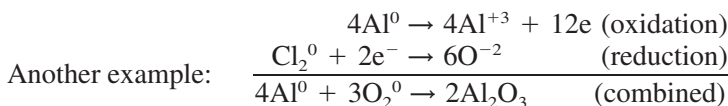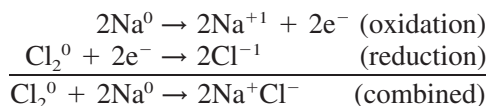
state of sodium has changed from the 0 state of the atom to the more positive $+1$ state of the ion.
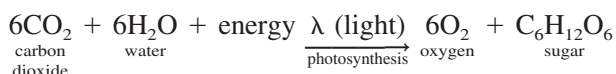
$$Na^0 \rightarrow Na^+ + e^-$$
sodium   sodium   electron
atom   ion

Simultaneously, each chlorine atom acquires an electron (becoming negatively charged) and is said to be reduced to a chloride ion.

$$Cl^0 + e^- \rightarrow Cl^-$$
chlorine   electron   chloride
atom   ion
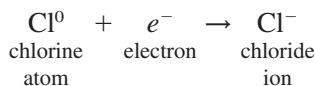
Redox reactions occur simultaneously and the degree of oxidation must be equal to the degree of reduction. When two sodium atoms are oxidized to Na^+ ions, an diatomic chlorine molecule is reduced to two Cl^- ions.

$$2Na^0 \rightarrow 2Na^{+1} + 2e^- \text{ (oxidation)}$$
$$\frac{Cl_2^0 + 2e^- \rightarrow 2Cl^{-1} \qquad\quad \text{(reduction)}}{Cl_2^0 + 2Na^0 \rightarrow 2Na^+Cl^- \qquad \text{(combined)}}$$

Another example:
$$4Al^0 \rightarrow 4Al^{+3} + 12e \text{ (oxidation)}$$
$$\frac{Cl_2^0 + 2e^- \rightarrow 6O^{-2} \qquad\qquad \text{(reduction)}}{4Al^0 + 3O_2^0 \rightarrow 2Al_2O_3 \qquad\quad \text{(combined)}}$$

During photosynthesis electrons and hydrogen atoms are transferred from water to carbon dioxide, thereby oxidizing the water to oxygen and reducing the carbon dioxide to form a sugar containing six carbon atoms:

$$6CO_2 + 6H_2O + \text{energy} \xrightarrow[\text{photosynthesis}]{\lambda \text{ (light)}} 6O_2 + C_6H_{12}O_6$$
carbon   water   oxygen   sugar
dioxide

In biology and soils, O_2, C, N, S and to a lesser extent, Fe and Mn, are the primary elements that carry out electron transfer (or energy transfer) via redox reactions. Other important redox reactions include the use of batteries, chlorination of drinking water, and corrosion of metals. Rust is the corrosion of iron to various reddish brown oxides when exposed to moisture and air. **Galvanizing,** which is a process of coating metals with zinc, protects them from corrosion.

### The Energy Factor in Chemical Reactions

Chemical reactions are either exothermic or **endothermic** processes. During a re-action a definite amount of chemical binding energy is changed into thermal (or internal) energy or vice versa. If a process is exothermic the total heat content of the products is lower than that of the reactants because of the loss of thermal energy.

Most **spontaneous reactions,** those that occur naturally or unassisted, give off energy (heat), thus are exothermic. If energy (heat) is added to the reaction, then it is endothermic. The products of an endothermic reaction must have a higher heat content than the reactants. For example, heat must be added to toast bread (this is endothermic and **nonspontaneous**), while in burning wood heat is given off and the reaction of burning continues by itself, thus is exothermic and spontaneous (once it is initially lit).

Molecules react with each other only when they collide with sufficient energy to (1) overcome the repulsive forces between their negatively charged electron orbitals and (2) break existing chemical bonds. The energy, called the **energy of activation,** is the amount of energy required to loosen bonds in molecules so they can cause a reaction. The energy of activation varies with the nature of the molecules: the more stable the substance, the more forceful the collision must be for a reaction to occur. Each chemical bond has a characteristic energy content, or bond energy. The higher the bond energy, the stronger the chemical bond and the greater the energy required to break it. The total bond energy of any molecule is the amount of energy required to break it into its constituent atoms.

In any given sample of molecules, some are moving with sufficient kinetic energy for a reaction to occur. At normal temperatures and pressures, the proportion of molecules with this energy may be so small that, for all practical purposes, the reaction does not take place. For example, hydrogen and oxygen gases do not combine spontaneously to form water when mixed at room temperature. The bonds of these molecular species must be broken, then new bonds between O and H atoms must be formed. Bond-breaking is an endothermic process and bond-forming is exothermic. The H and O molecules acquire enough energy to break the bonds between their atoms when the molecules collide and water is formed. Conversely, when atoms of H and O unite to form molecules of water, energy is released (exothermic). The amount of energy released is sufficient to provide the necessary activation energy for further H and O collisions to form water, and this "chain reaction" continues until either H or O sources are used up.

Reaction rates can be increased by increasing the likelihood of sufficiently forceful collisions between molecules. It appears that an initial energy "kick" (or activation) is needed to start the reaction. This can be achieved by: **raising the temperature,** thereby increasing the average velocity at which the molecules move, increasing their energy, and increasing the likelihood of their colliding with sufficient force to react. The use of heat to drive a chemical reaction is common in laboratories and in industry. **High pressure** and increasing the concentration of reaction molecules are additional techniques used to increase the rate of reactions. Increasing pressure increases the frequency of collision between reactants, thus increasing the reaction rate. An increase in pressure of a gas is similar to an increase in the concentration of the gas. **Catalysts** (commonly found as enzymes in plants) are used to increase the rates of reactions by lowering the energy of activation necessary to start a reaction and are shown above or below the arrow in chemical equations. For example, the reactions of A and B to form AB may be difficult because of a high energy of activation, but an alternative set of reactions may be possible, such as:

$$A + D \rightarrow AD$$

$$AD + B \rightarrow AB + D$$
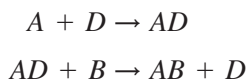
The energies of activation for A and D and for AD and B are both low. A substance such as D is a catalyst since it permits a reaction to occur rapidly at low temperature. Catalysts work in various ways but in general they form a weak complex with the reactants and after the energy barrier is passed, the catalyst is regenerated in its original state. A catalyst is not consumed during a reaction, thus only very small amounts are usually required. For example, if potassium chlorate is heated strongly it decomposes into potassium chloride and oxygen. However, if certain catalysts such as manganese dioxide are mixed with potassium chlorate, oxygen is released at a much lower temperature and at a more rapid rate. The manganese dioxide does not furnish the oxygen, it only speeds up the reaction.

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2\uparrow$$
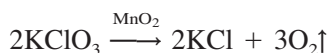
Living systems such as plants cannot use extreme temperatures and pressures to increase reaction rates, and the concentrations of reacting substances are often very low. Catalysts called **enzymes** are used by all living organisms to lower activation energies and increase rates.

The energy changes that occur in chemical reactions can be measured, and the relationships among various forms of energy are the bases for the science of **thermodynamics.** Consider a common respiration reaction where glucose is completely oxidized (or combusted to form carbon dioxide and water) represented by the following equation:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + energy\ (heat)$$
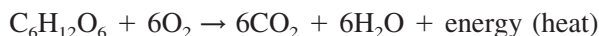
This reaction releases energy in the form of heat to its surroundings. The release of heat can be measured precisely and is expressed:

$$\Delta H = -673\ kilocalories\ per\ mole\ of\ glucose$$

where ΔH is the change in heat content. The negative value indicates that heat is released and thus is an exothermic reaction. Endothermic reactions require energy (heat) and have positive ΔH values.

A calorie is defined as the amount of heat necessary to raise the temperature of 1 gram of water by 1°C; (1,000 calories = 1 kilocalorie = 4,184 Joules, another means of expressing energy). A reaction that liberates heat, such as glucose combustion, is *exothermic. Endothermic* reactions require heat (or energy) to occur. In the case of glucose formation via photosynthesis, the energy source is the sun. Heat serves to increase the motion of molecules, which increases the frequency of collisions between reactants. In general, the rate of a reaction doubles for each 10°C (18 F) increase in temperature. Once an exothermic reaction begins, it often becomes self-sustaining by the heat energy it produces, like the burning of a piece of paper once a match starts the flame.

Plants cannot convert a portion of the energy generated by the digestion of food to work. Instead, plants transfer the energy, in each of many discrete steps, in the form of chemical-bond energy. A series of coupled reactions takes place in which, at each stage, a low-energy molecule from the surroundings is converted into a relatively high-energy molecule at the expense of the free energy of the oxidation. Figure 1-8 is an example of this stepwise transfer of energy involved in **photosynthesis** through the **Z-scheme.** Energy is provided by red and orange light from sunlight, followed by a series of coupled reactions where a group of atoms (e.g., the phosphate group associated with adenosine triphosphate [ATP] and adenosine diphosphate [ADP]) are transferred from one molecule to another down the chain, acting as an energy carrier. Not only is the energy transferred efficiently in the oxidation process, new high-energy species (such as ATP and NADP) are formed, and these can enter into other vital reactions elsewhere in the organism (such as the Calvin cycle). Plants appear green because red, orange, and violet light bands in light are absorbed by leaf tissue while green, yellow, and blue light bands are reflected, causing the leaf to appear green to the eyes.

Every spontaneous reaction increases the disorder or randomness (called **entropy**). Generally, entropy increases as a substance changes from solid to liquid to
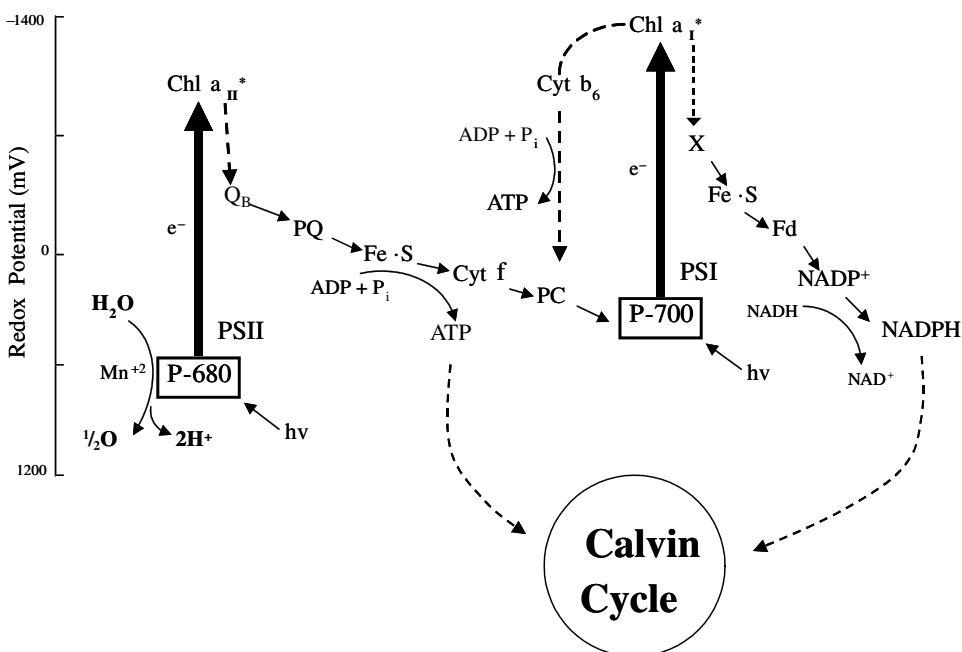

Figure 1-8. Electron (e^-) transport in the chloroplasts of higher plants (also known as the **Z-scheme**). Individual components are positioned according to their redox potential (electron donating or accepting properties). The diagram illustrates the antennae chlorophyll molecules feeding energy from sunlight (hv) into the special chlorophylls (Chl $a_{I\ and\ II}$) associated with photosystem I (indicated as PSI) and photosystem II (PSII). The broken line indicates a cyclic electron flow in the PSI system allowing electrons to be recycled through a quencher (Q_B), iron-sulfur protein (Fe·S), cytochrome f (Cyt f), cytochrome b_6 (Cyt b_6), plastoquinone (PQ), and ferredoxin (Fd) under special conditions. Almost all of the molecular oxygen in the atmosphere is a product of photosynthesis.

gas. Entropy increases especially from liquid to gas because of the large increase in volume. Entropy also increases downward within a group of the periodic table, as the temperature of the substance increases and as the number of atoms bonded together increases for similar structures.

PRACTICE PROBLEMS

1. What is an *atom*? (*the smallest particle that can exist as an element*).
2. What is a *molecule*? (*the smallest particle of a substance that retains properties of that substance*).
3. What is an *element*? (*a substance that cannot be broken into a simpler substance by chemical change*).
4. How does a *mixture* differ from a *compound*? (*elements in a compound are chemically combined; they cannot be separated by physical means, as the constituents of a mixture can*).
5. Which is the stronger acid, HPO_3 or HPO_4? (*HPO_4*).
6. Determine the oxidation number of the underlined element in each compound.
   a. $\underline{Cu}Cl$ (*$^+1$*)
   b. $\underline{Fe}O$ (*$^+2$*)
   c. $\underline{Fe}_2O_3$ (*$^+3$*)
   d. $\underline{Sn}F_4$ (*$^+4$*)
7. What is 1 meq of aluminum (Al^{+3})? (*9 mg*).
8. What is the number of atoms in 2.25 mole of Cu? (*1.35×10^{24}*).
9. (a) How many grams are in 1.00 mole H_2S? (*34 g*).
   (b) How many atoms and molecules are in 10.3 g H_2S? (*atoms = 5.45 × 10^{23}; molecules = 1.82 × 10^{23}*).
10. How many atoms are present in 2 moles of water molecules? (*2 × 3 × [6.02 × 10^{23}] = 3.612 × 10^{24} atoms*).
11. What is meant by the term *mole*? (*chemical unit to "count" atoms and molecules. There are 6.02 × 10^{23} particles in a mole*).
12. What is the significance of *Avogadro's Number* (6.02 × 10^{23})? (*by knowing exactly the number of molecules in one mole, one can calculate relative weights of one molecule of an element*).
13. How many bricks would be found in 2 moles of bricks? (*2 × [6.02 × 10^{23}] = 12.04 × 10^{23} bricks = 1.204 × 10^{24}*).
14. How many moles are in each: (a) 2,000 g of water, (*111.0 moles*); (b) 14 g of CO_2, (*0.318 mole*). (c) 24 g of O_2, (*0.75 mole*); and, (d) 92 g of ethyl alcohol (C_2H_5OH)? (*2 moles*).
15. What are the number of moles in: (a) 2.53 × 10^{22} atom of Al? (*0.042*); and (b), 14.3 g of $NaC_{18}H_{35}O_2$ (soap)? (*0.0467*).
16. What information does a formula such as $PbCl_2$ provide? (*two types of atoms are present; Pb and Cl; Pb and Cl atoms are in a 1:2 ratio; there is one mole of $PbCl_2$ molecules, and 278.1 g of $PbCl_2$*).

17. Consider the formula for table sugar (or sucrose), $C_{12}H_{22}O_{11}$. What does it indicate in regard to:

    a. types of atoms present? (*three types—carbon, hydrogen, and oxygen*).

    b. number of each type of atom present? (*12 C atoms; 22 H atoms; 11 O atoms*).

    c. moles of molecules present? (*1 mole of $C_{12}H_{22}O_{11}$ molecules*).

    d. weight (g) of one mole of sugar molecules? (*C = 12 × 12.00 = 144.0; H = 22 × 1.00 = 22.0; O = 11 × 16.00 = 176.0; 144 + 22 + 176 = 342 g*).

18. How many moles of *molecules* and *atoms* are represented in the formula P_4? (*1 mole of P_4 molecules and 4 moles of phosphorus [P] atoms*).

19. What is the percent composition of H and O in H_2O? (*11.1% H, 88.9% O*).

20. What is the percent composition of $Ca(NO_3)_2$? (*24.5% Ca; 17.1% N; 58.5% O*).

21. What is the percent composition of glucose ($C_6H_{12}O_6$)? (*40% C; 6.71% H; 53.29% O*).

22. How many kg of iron can be removed from 639 kg of Fe_2O_3? (*Fe_2O_3 is 70% Fe, therefore, 447 kg Fe*).

23. Determine the empirical formula of the compound with 29.1% Na, 40.5% S, and 30.4% O. (*$Na_2S_2O_3$*).

24. What is meant by *molecular weight*? (*the weight, in grams, of one mole [6.02 × 10²³ molecules] of a compound*).

25. What is the weight of:

    a. $6.02 × 10^{23}$ atoms of N? (*14.0 g*).

    b. one atom of N? (*$2.33 × 10^{-23}$ g*).

26. What is the weight of:

    a. 1 mole of iron (Fe) atoms? (*1 m × 55.8 g/m = 55.8 g*).

    b. 1 atom of Fe? (*55.8 g/m ÷ 6.02 × 10²³ molecules/m = 9.27 × 10⁻²³g*).

27. Calculate the formula weights of:

    a. KNO_3 (potassium nitrate) (*101.8 g*).

    b. $CO(NH_2)_2$ (urea) (*60.04 g*).

    c. NaOCl (bleach) (*74.44 g*).

    d. K_2SO_4 (potassium sulfate) (*174.3 g*).

28. Find molarities of the following:

Solution	Density (g/mL)	Weight Percent	Molarity
KOH	1.344	35	(8.40)
HNO_3	1.334	54	(11.45)
H_2SO_4	1.834	95	(17.74)
$Al_2(SO_4)_3$	1.253	22	(0.805)

29. What is the excess reagent when 3.1 mole SO_2 reacts with 2.7 mole O_2? (*1.6 mole O_2 is required, thus, SO_2 is in excess*).

30. (a) How many liters of CO_2 at standard temperature and pressure are consumed by a plant in producing 454 g of glucose by the following photosynthesis reaction, and (b) how many liters of air are needed to supply the required CO_2 in part (a) assuming air is 0.040 percent CO_2 by volume? [(a) *338 liters,* (b) *8.45 $\times$ 10^5 liters*].

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

31. In the production of ammonium sulfate fertilizer, the following reactions occurs. If 22.7 g NH_3 and 54.8 g H_2SO_4 are used: (a) Which reactant is limiting, (b) which reactant will be left over and how much (grams), and (c) how many grams of ammonium sulfate can be formed? [(a) *H_2SO_4* (b) *3.7 g NH_3* (c) *73.8 g*].

$$6NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

32. (a) How many moles of H_2SO_4 are needed to completely react with 0.15 mole NaOH, and (b) How many grams of NaOH are needed to react with excess H_2SO_4 to prepare 60 g of Na_2SO_4? [(a) *0.075 mol H_2SO_4;* (b) *33.8 g NaOH*].

33. How many moles of $KClO_3$ are in 500 mL of 0.150 *M* solution? (*0.075 moles*).

34. How many grams of $BaCl_2$ are needed to prepare 200 mL of a 0.500 *M* solution? (*20.8 g*).

35. How many grams of NaOH are needed to prepare 1 liter of 0.20 *M* NaOH? (*8.0 g NaOH*).

36. What is the molar concentration of hydrochloric acid (HCl) with a density of 1.2 g/mL and is 36% HCl by mass? (*12 M*).

37. How much H_2SO_4 with a density of 1,840 g/L is needed to prepare 0.5 liter of 6.0 *M* solution? (*0.160 liter or 160 mL*).

38. How many grams of sucrose, $C_{12}H_{22}O_{11}$, are needed to make 300 mL of a 0.50 *M* solution? (*51.3 g*).

39. How many mL of 2.0 *M* NaBr are needed to prepare 300 mL of 0.75 *M* NaBr? (*112.5 mL*).

40. What is the molarity of a 200 mL solution prepared by adding water to 10 g of KCl? (*0.670 M*).

41. How many moles of sodium hydroxide (NaOH) are needed to completely neutralize 1 liter of the following?
   a. 1 *M* hydrochloric acid, HCl (*1*).
   b. 1 *M* phosphoric acid, H_3PO_4 (*3*).
   c. 1 *M* sulfuric acid, H_2SO_4 (*2*).

42. Determine the number of equivalents per mole of the following:

    a. H_2O (*2*).

    b. $HClO_4$ (*1*).

    c. K_2SO_4 (*2*).

    d. $CaCl_2$ (*2*).

    e. HF (*1*).

43. What is the equivalent weight of KOH? (*56.1 g*).

44. How many grams are in 1 equivalent of each of the following?

    a. $Ca(NO_3)_2$ (*82 g*).

    b. Zn (*32.7 g*).

    c. HCO_3^- (*61.0 g*).

    d. KCl (*74.6 g*).

    e. $Al_2(SO_4)_3$ (*57.0 g*).

45. How many equivalents are in 20.5 g of sulfurous acid, H_2SO_3? (*0.50 equivalents*).

46. What is the equivalent weight of HSO_4^-? (*97 g*).

47. Convert 97.5 mg of K^+ to milliequivalent weight. (*2.5 meq K^+*).

48. A soil sample from a coastal golf course fairway was analyzed and found to have a sodium (Na) concentration of 8,000 ppm (mg/kg). How many meq Na^+/100 g does this soil contain? (*34.8 meq/100 g. This would be considered very high and only the most salt tolerant turfgrasses would be expected to survive*).

49. Balance the following equations and tell what type reaction each represents.

    a. zinc + chlorine → zinc chloride (*$Zn + Cl_2 → ZnCl_2$; combination*).

    b. mercury(II) oxide → mercury + oxygen (*$2HgO → 2Hg + O_2$; decomposition*).

    c. calcium carbonate + sulfuric acid (H_2SO_4) → calcium sulfate + water + carbon dioxide (*$CaCO_3 + H_2SO_4 → CaSO_4 + H_2O + CO_3$; double replacement*).

    d. sodium hydrogen carbonate → sodium carbonate + water + carbon dioxide

       (*$2NaHCO_3 + Na_2CO_3 + H_2O + CO_2$; decomposition*).

    e. Al_2O_3 → Al + O_2 (*$2Al_2O_3 → 4Al + 3O_2$; decomposition*).

    f. Fe + Br_2 → $FeBr_3$ (*$2Fe + 2Br_3 → 2FeBr_3$; combination*).

    g. Zn + HCl → H_2 + $ZnCl_2$ (*$Zn + 2HCl → H_2 + ZnCl_2$; single replacement*).

    h. $AgNO_3$ + AlI_3 → AgI + $Al(NO_3)_3$ (*$3AgNO_3 + AlI_3 → 3AgI + Al(NO_3)_3$; double replacement*).

    i. NaOH + H_2SO_4 → Na_2SO_4 + H_2O (*$2NaOH + H_2SO_4 → Na_2SO_4 + 2H_2O$; double replacement*).

50. Balance the following equations and tell what type reaction each represents.

    a. zinc + chlorine → zinc chloride (*$Zn + Cl_2 → ZnCl_2$; combination*).

    b. mercury(II) oxide → mercury + oxygen (*$2HgO → 2Hg + O_2$; decomposition*).

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d. sodium hydrogen carbonate → sodium carbonate + water + carbon dioxide (*$2NaHCO_3$ → Na_2CO_3 + H_2O + CO_2; decomposition*).

e. Al_2O_3 → Al + O_2 (*$2Al_2O_3$ → $4Al$ + $3O_2$; decomposition*).

f. Fe + Br_2 → $FeBr_3$ (*$2Fe$ + $2Br_3$ → $2FeBr_3$; combination*).

g. Zn + HCl → H_2 + $ZnCl_2$ (*Zn + $2HCl$ → H_2 + $ZnCl_2$; single replacement*).

h. $AgNO_3$ + AlI_3 → AgI + $Al(NO_3)_3$ (*$3AgNO_3$ + AlI_3 → $3AgI$ + $Al(NO_3)_3$; double replacement*).

i. sodium oxide + water → sodium hydroxide (*Na_2O + H_2O → $2NaOH$: combination*).

j. NaOH + H_2SO_4 → Na_2SO_4 + H_2O (*$2NaOH$ + H_2SO_4 → Na_2SO_4 + $2H_2O$; double replacement*).

k. sulfurous acid (aq) → water + sulfur dioxide (*H_2SO_4 → H_2O + SO_2: decomposition*).

l. Fe + $CuSO_4$ → $FeSO_4$ + Cu (*balanced; single replacement*).

m. aluminum + hydrochloric acid → aluminum chloride + hydrogen (*2Al + 6HCl → $2AlCl_3$ + $3H_2$; single replacement*).

n. hydrochloric acid + magnesium hydroxide → magnesium chloride + water (*$2HCl$ + $Mg(OH)_2$ → $MgCl_2$ + $2H_2O$; double replacement*).

51. For the following reactions, determine which substance is oxidized and which is reduced.

a. Zn + 2HCl → $ZnCl_2$ + H_2 (*zinc is oxidized as its oxidation number changes from 0 to +2; hydrogen is reduced as its oxidation number changes from +1 to 0; chlorine is unchanged*).

b. C + O_2 → CO_2 (*carbon is oxidized; oxygen is reduced*).

c. 2HgO → 2Hg + O_2 (*mercury oxidation changes from +2 to 0, thus, is reduced; the oxygen changes from −2 to 0, thus, is oxidized*).