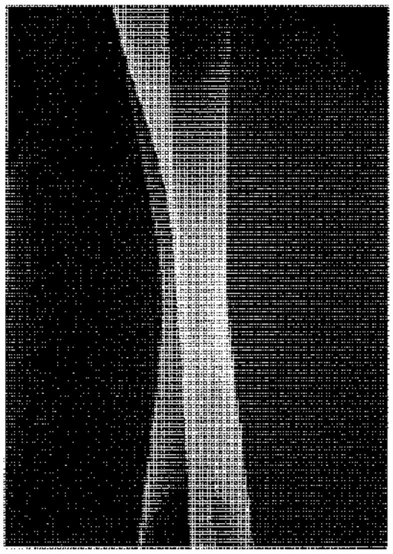
Steven S. Zumdahl
UNIVERSITY OF ILLINOIS

Chemistry



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To my parents and to Eunice, Whitney, and Leslie.

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CHAPTER TWO

Atoms, Molecules, and Ions

CONTENTS

To fully appreciate a science like chemistry, we must understand something of its origins. In this chapter we will see how chemistry developed, paying particular attention to the crucial experiments and fundamental laws that form the basis of modern chemistry. We will also consider chemical nomenclature and introduce some of the most important chemical concepts.

2.1 The Early History of Chemistry

PURPOSE

☐ To give a brief account of early chemical discoveries.

Chemistry has been important since ancient times. The processing of natural ores to produce metals for ornaments and weapons and the use of embalming fluids are two examples of chemical phenomena that were utilized prior to 1000 B.C.

The Greeks were the first to try to explain why chemical changes occur. By about 400 B.C. they had proposed that all matter was composed of four fundamental substances: fire, earth, water, and air. The Greeks also considered the question of whether matter is continuous, and thus infinitely divisible into smaller pieces, or composed of small indivisible particles. One supporter of the latter position was Democritus, who used the term *atomos* (which later became *atoms*) to describe these ultimate particles. However, because the Greeks had no experiments to test their ideas, no definitive conclusion about the divisibility of matter was reached.

The Alchemists, an oil on slate painting by Jan van der Straet in 1570.

The next 2000 years of chemical history were dominated by a pseudoscience called **alchemy.** Alchemists were often mystics and fakes who were obsessed with the idea of turning cheap metals into gold. However, this period also saw important discoveries: elements such as mercury, sulfur, and antimony were discovered, and alchemists learned how to prepare the mineral acids

The foundations for modern chemistry were laid in the sixteenth century with the development of systematic metallurgy (extraction of metals from ores) by a German, Georg Bauer, and the medicinal application of minerals by a Swiss alchemist called Paracelsus.

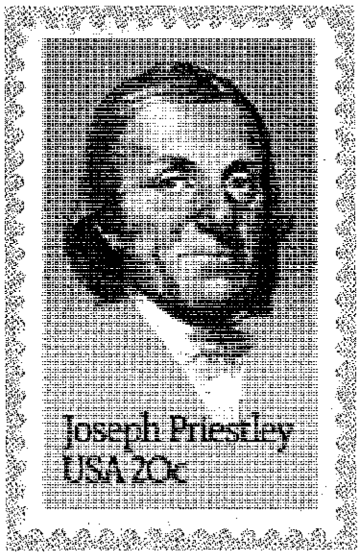
The first person to perform truly quantitative physical experiments was Robert Boyle (1627–1691), who carefully measured the relationship between the pressure and volume of gases. When Boyle published his book, *The Sceptical Chemist,* in 1661, the quantitative sciences of physics and chemistry were born. In addition to his results on the quantitative behavior of gases, Boyle's other major contribution to chemistry consisted of his ideas about the chemical elements. Boyle held no preconceived notion about the number of elements. In his view a substance was an element unless it could be broken down into two or more simpler substances. As Boyle's experimental definition of an element became generally accepted, the list of known elements began to grow, and the Greek system of four elements finally died. Although Boyle was an excellent scientist, he was not always right. For example, he clung to the alchemist's views that metals were not true elements and that a way would eventually be found to change one metal to another.

The phenomenon of combustion evoked intense interest in the seventeenth and eighteenth centuries. The German chemist Georg Stahl (1660–1734) suggested that a substance he called phlogiston flowed out of the burning material. Stahl postulated that a substance burning in a closed container eventually stopped burning, because the air in the container became saturated with phlogiston. Oxygen gas, discovered by Joseph Priestley (1733–1804), an English clergyman and scientist (Fig. 2.1), was found to support vigorous combustion and was thus supposed to be low in phlogiston. In fact, oxygen was originally called "dephlogisticated air."

Figure 2.1

Joseph Priestley was born in England on March 13, 1733, and showed a great talent for science and languages from an early age. Priestley performed many important scientific experiments, among them the discovery that the gas produced by the fermentation of grain (later identified as carbon dioxide) could be dissolved in water to produce the pleasant drink called *seltzer.* Also, as a result of meeting Benjamin Franklin in London in 1766, Priestley became interested in electricity and was the first to observe that graphite was an electrical conductor. However, Priestley's greatest discovery occurred in 1774 when he isolated oxygen by heating mercuric oxide.

Because of his nonconformist political views (he supported both the American and French revolutions), he was forced to leave England (a mob burned his house in Birmingham in 1791). He spent his last decade peacefully in the United States, and died in 1804.



2.2 Fundamental Chemical Laws

PURPOSE

☐ To describe and illustrate the laws of conservation of mass, definite proportion, and multiple proportions.

By the late eighteenth century, combustion had been studied extensively; the gases carbon dioxide, nitrogen, hydrogen, and oxygen had been discovered; and the list of elements continued to grow. However, it was Antoine Lavoisier (1743–1794), a French chemist (Fig. 2.2), who finally explained the true nature of combustion, thus clearing the way for the tremendous progress that was made near the end of the eighteenth century. Lavoisier, like Boyle, regarded measurement as the essential operation of chemistry. His experiments, in which he carefully weighed the reactants and the products of various reactions, showed that *mass was neither created nor destroyed.* Lavoisier's discovery of this **law of conservation of mass** was the basis for the developments in chemistry in the nineteenth century.

Lavoisier's quantitative experiments showed that combustion involved oxygen (which Lavoisier named), not phlogiston. He also discovered that life was supported by a process that also involved oxygen and was similar in many ways to combustion. In 1789 Lavoisier published the first modern chemistry textbook, *Elementary Treatise on Chemistry,* in which he presented a unified picture of the chemical knowledge assembled up to that time. Unfortunately, in the same year the text was published, the French Revolution broke out. Lavoisier, who had been associated with collecting taxes for the government, was executed on the guillotine as an enemy of the people in 1794.

After 1800 chemistry was dominated by scientists who, following Lavoisier's lead, performed careful weighing experiments to study the course of chemical reactions and to determine the composition of various chemical compounds. One of these chemists, a Frenchman, Joseph Proust (1754–1826), showed that *a given*

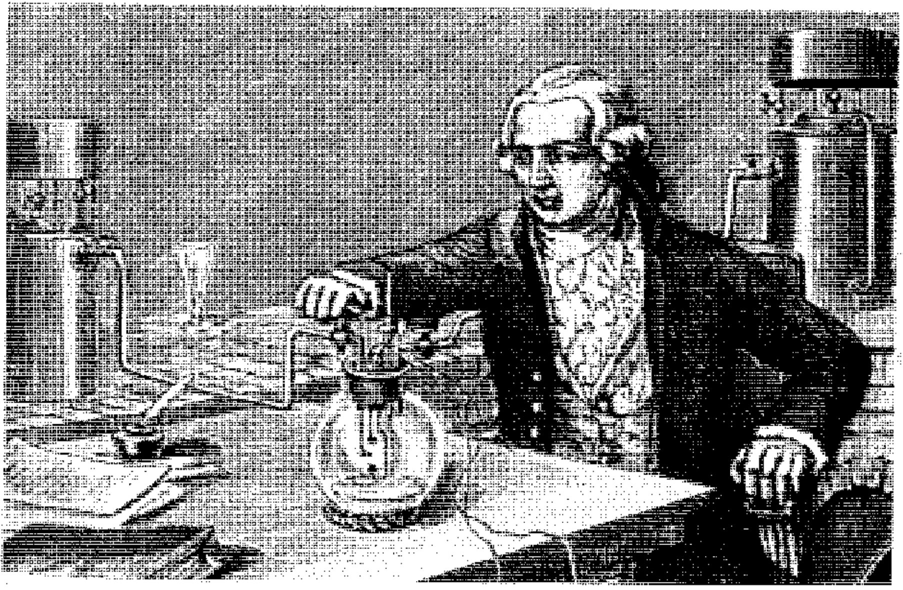


Figure 2.2

Antoine Lavoisier was born in Paris on August 26, 1743. Although Lavoisier's father wanted his son to follow him into the legal profession, young Lavoisier was fascinated by science. From the beginning of his scientific career, Lavoisier recognized the importance of accurate measurements. His careful weighings showed that mass was conserved in chemical reactions and that combustion involves reaction with oxygen. Also, he wrote the first modern chemistry textbook. It is not surprising that Lavoisier is often called the father of modern chemistry.

To help support his scientific work, Lavoisier invested in a private tax-collecting firm and married the daughter of one of the company executives. His connection to the tax collectors proved fatal, for radical French revolutionaries demanded his execution, which occurred on the guillotine on May 8, 1794.

compound always contains exactly the same proportion of elements by weight. For example, Proust found that the substance copper carbonate is always 5.3 parts copper to 4 parts oxygen to 1 part carbon (by mass). The principle of the constant composition of compounds, originally called Proust's law, is now known as the **law of definite proportion.**

Figure 2.3

John Dalton (1766–1844), an Englishman, began teaching at a Quaker school when he was 12. His fascination with science included an intense interest in meteorology (he kept careful daily weather records for 46 years), which led to an interest in the gases of the air and their ultimate components, atoms. Dalton is best known for his atomic theory, in which he postulated that the fundamental differences among atoms are their masses. He was the first to prepare a table of relative atomic weights.

Dalton was a humble man with several apparent handicaps: he was poor; he was not articulate; he was not a skilled experimentalist; and he was color-blind, a terrible problem for a chemist. In spite of these disadvantages, he helped to revolutionize the science of chemistry.

Proust's discovery stimulated John Dalton (1766–1844), an English schoolteacher (Fig. 2.3), to think about atoms. Dalton reasoned that if elements were composed of tiny individual particles, a given compound should always contain the same combination of these atoms. This concept explained why the same relative masses of elements were always found in a given compound.

But Dalton discovered another principle that convinced him even more of the existence of atoms. He noted, for example, that carbon and oxygen formed two different compounds that contained different relative amounts of carbon and oxygen as shown by the following data:

	Weight of oxygen that combines with 1 g of carbon
Compound I	1.33 g
Compound II	2.66 g

Dalton noted that compound II contained twice as much oxygen per gram of carbon as compound I, a fact that could be easily explained in terms of atoms. Compound I might be CO, and compound II might be CO_2. This principle, which was found to apply to compounds of other elements as well, became known as the **law of multiple proportions:** *when two elements form a series of compounds, the ratios of the masses of the second element that combine with 1 gram of the first element can always be reduced to small whole numbers.*

To make sure the significance of this observation is clear, in Sample Exercise 2.1 we will consider data for a series of compounds consisting of nitrogen and oxygen.

Sample Exercise 2.1

The following data were collected for several compounds of nitrogen and oxygen:

	Mass of nitrogen that combines with 1 g of oxygen
Compound I	1.750 g
Compound II	0.8750 g
Compound III	0.4375 g

Show how these data illustrate the law of multiple proportions.

Solution

For the law of multiple proportions to hold, the ratios of the masses of nitrogen combining with 1 gram of oxygen in each pair of compounds should be small whole numbers. We therefore compute the ratios as follows:

$$\frac{\text{I}}{\text{II}} = \frac{1.750}{0.875} = \frac{2}{1}$$

$$\frac{\text{II}}{\text{III}} = \frac{0.875}{0.4375} = \frac{2}{1}$$

$$\frac{\text{I}}{\text{III}} = \frac{1.750}{0.4375} = \frac{4}{1}$$

These results support the law of multiple proportions.

The significance of the data in Sample Exercise 2.1 is that compound I contains twice as much nitrogen (N) per gram of oxygen (O) as does compound II and that compound II contains twice as much nitrogen per gram of oxygen as does compound III. In terms of the numbers of atoms combining, these data can be explained by any of the following formulas*:

Compound I	N_2O		NO		N_4O_2
Compound II	NO	or	NO_2	or	N_2O_2
Compound III	NO_2		NO_4		N_2O_4

In fact an infinite number of other possibilities exists. Dalton could not deduce absolute formulas from the available data on relative masses. However, the data on the composition of compounds in terms of the relative masses of the elements supported his hypothesis that each element consisted of a certain type of atom and that compounds were formed from specific combinations of atoms.

2.3 Dalton's Atomic Theory

PURPOSE

☐ To describe Dalton's theory of atoms and show the significance of Gay-Lussac's experiments.

In 1808 Dalton published *A New System of Chemical Philosophy,* in which he presented his theory of atoms:

1. *Each element is made up of tiny particles called atoms.*
2. *The atoms of a given element are identical; the atoms of different elements are different in some fundamental way or ways.*
3. *Chemical compounds are formed when atoms combine with each other. A given compound always has the same relative numbers and types of atoms.*
4. *Chemical reactions involve reorganization of the atoms—changes in the way they are bound together. The atoms themselves are not changed in a chemical reaction.*

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*Subscripts are used to show the numbers of atoms present. The number 1 is understood and thus is not written. The symbols for the elements and the writing of chemical formulas will be illustrated further in Sections 2.6 and 2.7.

It is instructive to consider Dalton's reasoning on the relative masses of the atoms of the various elements. In Dalton's time water was known to be composed of the elements hydrogen and oxygen, with 8 grams of oxygen present for every 1 gram of hydrogen. If the formula for water were OH, an oxygen atom would have to have 8 times the mass of a hydrogen atom. However, if the formula for water were H_2O (two atoms of hydrogen for every oxygen atom), this would mean that each atom of oxygen is 16 times as heavy as *each* atom of hydrogen (since the ratio of the mass of one oxygen to that of *two* hydrogens is 8 to 1). Because the formula for water was not then known, Dalton could not specify the relative masses of oxygen and hydrogen unambiguously. To solve the problem, Dalton made a fundamental assumption: he decided that nature would be as simple as possible. This assumption led him to conclude that the formula for water should be OH. He thus assigned hydrogen a mass of 1 and oxygen a mass of 8.

Using similar reasoning for other compounds, Dalton prepared the first table of **atomic masses** (called **atomic weights** by chemists, since mass is often determined by comparison to a standard mass—a process called *weighing*). Many of the masses were later proved to be wrong because of Dalton's incorrect assumptions about the formulas of certain compounds, but the construction of a table of masses was an important step forward.

Although not recognized as such for many years, the keys to determining absolute formulas for compounds were provided in the experimental work of the French chemist Joseph Gay-Lussac (1778–1850) and by the hypothesis of an Italian chemist named Amadeo Avogadro (1776–1856). In 1809 Gay-Lussac performed experiments in which he measured (under the same conditions of temperature and pressure) the volumes of gases that reacted with each other. For example, Gay-Lussac found that 2 volumes of hydrogen react with 1 volume of oxygen to form 2 volumes of gaseous water and that 1 volume of hydrogen reacts with 1 volume of chlorine to form 2 volumes of hydrogen chloride. These results are represented schematically in Fig. 2.4

In 1811 Avogadro interpreted these results by proposing that, *at the same temperature and pressure, equal volumes of different gases contain the same number of particles*. This assumption (called **Avogadro's hypothesis**) makes sense if the distances between the particles in a gas are very great compared to the sizes of the particles. Under these conditions the volume of a gas is determined by the number of molecules present, not by the size of the individual particles.

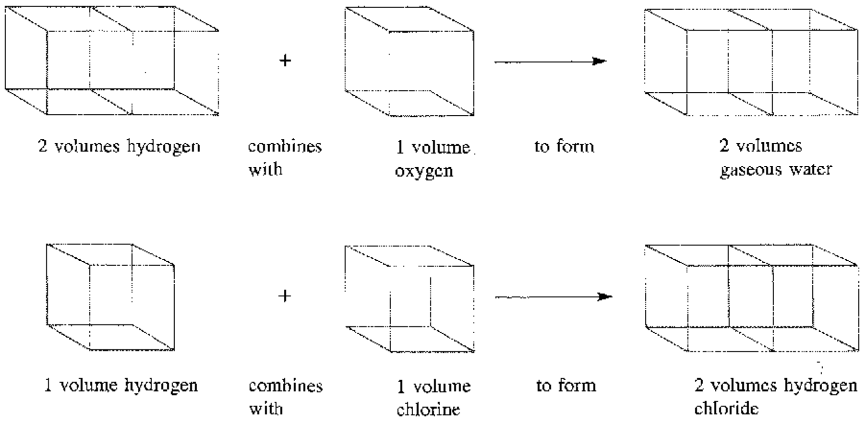

Figure 2.4

A representation of some of Gay-Lussac's experimental results on combining gas volumes.

If Avogadro's hypothesis is correct, Gay-Lussac's result,

2 volumes of hydrogen react with 1 volume of oxygen
→ 2 volumes of water vapor

can be expressed as follows:

2 molecules* of hydrogen react with 1 molecule of oxygen
→ 2 molecules of water

These observations can best be explained by assuming that gaseous hydrogen, oxygen, and chlorine are all composed of diatomic (two-atom) molecules: H_2, O_2, and Cl_2, respectively. Gay-Lussac's results can then be represented as shown in Fig. 2.5. (Note that this reasoning suggests that the formula for water is H_2O, not OH as Dalton believed.)

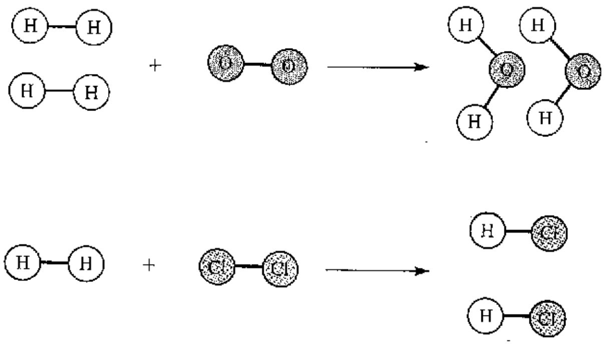

Figure 2.5

A representation of combining gases at the molecular level. The circles represent atoms in the molecules.

Unfortunately, Avogadro's interpretations were not accepted by most chemists and a half-century of confusion followed, in which many different assumptions were made about formulas and atomic masses.

During the nineteenth century painstaking measurements were made of the masses of various elements that combined to form compounds. From these experiments a list of relative atomic masses could be determined. One of the chemists involved in adding to this list was a Swede named Jöns Jakob Berzelius (1779–1848), who discovered the elements cerium, selenium, silicon, and thorium and developed the modern symbols for the elements used in writing the formulas of compounds.

The work of Berzelius is described further in the Chemical Impact feature at the end of this chapter.

2.4 Early Experiments to Characterize the Atom

PURPOSE

☐ To summarize the experiments that characterized the structure of the atom.

Dalton's atomic theory caused chemistry to become more systematic and more sensible. The concept of atoms was clearly a good idea, and scientists became very interested in the structure of the atom.

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*A molecule is a collection of atoms (see Section 2.6).

The Electron

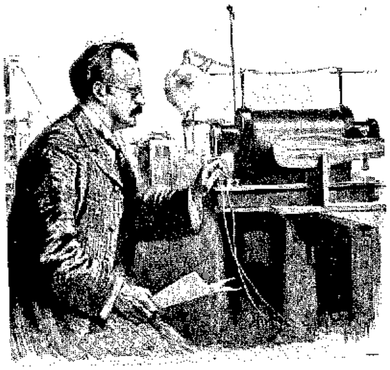


Figure 2.6

J. J. Thomson (1856–1940) was an English physicist at Cambridge University. He received the Nobel Prize in physics in 1906.

The first important experiments that led to an understanding of the composition of the atom were done by the English physicist J. J. Thomson (Fig. 2.6), who studied electrical discharges in partially evacuated tubes called *cathode-ray tubes* (Fig. 2.7) during the period from 1898 to 1903. Thomson found that, when high voltage was applied to the tube, a "ray" he called a **cathode ray** (because it emanated from the negative electrode, or cathode) was produced. Because this ray was produced at the negative electrode and was repelled by the negative pole of an applied electric field (see Fig. 2.8), Thomson postulated that the ray was a stream of negatively charged particles, which he called **electrons.** By experiments in which he measured the deflection of the beam of electrons in a magnetic field, Thomson determined the *charge-to-mass ratio* of an electron:

$$\frac{e}{m} = -1.76 \times 10^8 \text{ C/g}$$

where e represents the charge on the electron in coulombs and m represents the electron mass in grams.

One of Thomson's primary goals in his cathode-ray tube experiments was to gain an understanding of the structure of the atom. He reasoned that, since electrons could be produced from electrodes made of various types of metals, *all* atoms must contain electrons. Since atoms were known to be electrically neutral, Thomson further assumed that atoms also must contain some positive charge. Thomson postulated* that an atom consisted of a diffuse cloud of positive charge with the negative electrons embedded randomly in it. This model, shown in Fig. 2.9, is often called the *plum pudding model* because the electrons are like raisins dispersed in a pudding (the positive charge cloud), as in plum pudding, a favorite English dessert.

In 1909 Robert Millikan (1868–1953), working at the University of Chicago, performed very clever experiments involving charged oil drops. These experiments allowed him to determine the magnitude of the electron charge (see Fig. 2.10). With this value and the charge-to-mass ratio determined by Thomson, Millikan was able to calculate the mass of the electron as 9.11×10^{-28} gram.

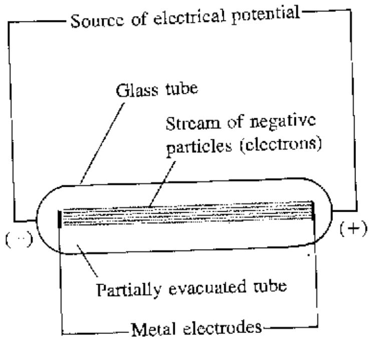


Figure 2.7

Schematic of a cathode-ray tube. A stream of electrons passes between the electrodes. The fast-moving electrons excite the gas in the tube, causing a glow between the electrodes.

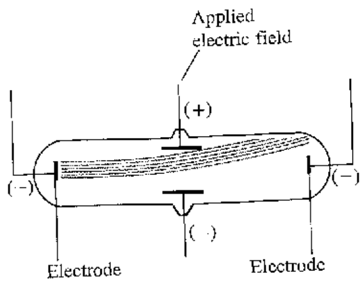
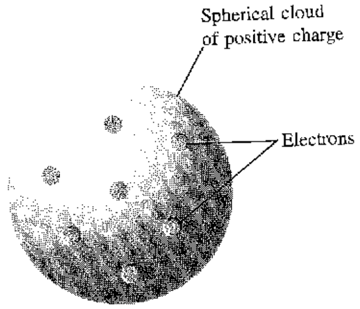


Figure 2.8

Deflection of cathode rays by an applied electric field.

Figure 2.9

One of the early models of the atom was Thomson's plum pudding model, in which the electrons were pictured as embedded in a positively charged spherical cloud, in the same way as raisins are distributed in an old-fashioned plum pudding.



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*Although J. J. Thomson is generally given credit for this model, the idea was apparently first suggested by the English mathematician and physicist William Thomson (better known as Lord Kelvin and not related to J. J. Thomson).

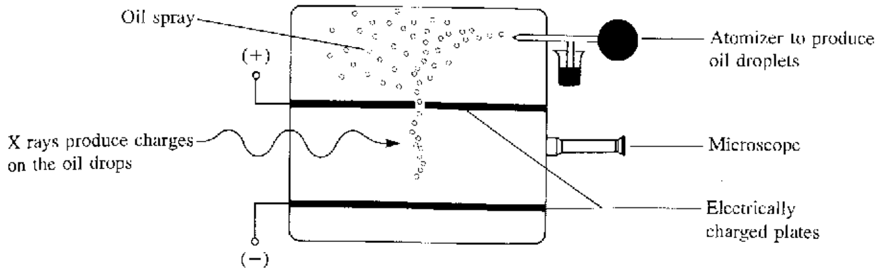

Figure 2.10

A schematic representation of the apparatus Millikan used to determine the charge on the electron. The fall of charged oil droplets due to gravity can be halted by adjusting the voltage across the two plates. The voltage and the mass of an oil drop can then be used to calculate the charge on the oil drop. Millikan's experiments showed that the charge on an oil drop is always a whole-number multiple of the electron charge.

Radioactivity

In the late nineteenth century, it was discovered that certain elements produce high-energy radiation. For example, in 1896 the French scientist Henri Becquerel found that a piece of a mineral containing uranium could produce its image on a photographic plate in the absence of light. He attributed this phenomenon to a spontaneous emission of radiation by the uranium, which he called **radioactivity.** Studies in the early twentieth century demonstrated three types of radioactive emission: gamma (γ) rays, beta (β) particles, and alpha (α) particles. A γ ray is high-energy "light"; a β particle is a high-speed electron; and an α particle has a 2+ charge, that is, a charge twice that of the electron and with the opposite sign. The mass of an α particle is 7300 times that of the electron. More modes of radioactivity are now known, and we will discuss them in Chapter 21. Here we will consider only α particles because they were used in some crucial early experiments.

The Nuclear Atom

In 1911 Ernest Rutherford (Fig. 2.11), who performed many of the pioneering experiments to explore radioactivity, carried out an experiment to test Thomson's plum pudding model. The experiment involved directing α particles at a thin sheet of metal foil, as illustrated in Fig. 2.12. Rutherford reasoned that, if Thomson's model were accurate, the massive α particles should crash through the thin foil like cannonballs through gauze, as shown in Fig. 2.13(a). He expected the α particles to travel through the foil, with, at the most, very minor deflections in their paths. The results of the experiment were very different from those Rutherford anticipated. Although most of the α particles passed straight through, many of the particles were deflected at large angles, as shown in Fig. 2.13(b), and some were reflected, never hitting the detector. This outcome was a great surprise to Rutherford. (He wrote that this result was comparable to shooting a howitzer at a piece of paper and having the shell reflected back.)

Rutherford knew from these results that the plum pudding model for the atom could not be correct. The large deflections of the α particles could only be caused by a center of concentrated positive charge, as illustrated in Fig. 2.13(b). Most of the α particles pass directly through the foil because the atom is mostly open space. The deflected α particles are those that had a "close encounter" with the positive center of the atom, and the few reflected α particles are those that made a "direct hit" on the much more massive positive center.

Figure 2.11

Ernest Rutherford (1871–1937) was born on a farm in New Zealand. In 1895 he placed second in a scholarship competition to attend Cambridge University, but was awarded the scholarship when the winner decided to stay home and get married. As a scientist in England, Rutherford did much of the early work on characterizing radioactivity. He named the α and β particles and the γ ray and coined the term *half-life* to describe an important attribute of radioactive elements. His experiments on the behavior of α particles striking thin metal foils led him to postulate the nuclear atom. He also invented the name *proton* for the nucleus of the hydrogen atom. He received the Nobel Prize in chemistry in 1908.

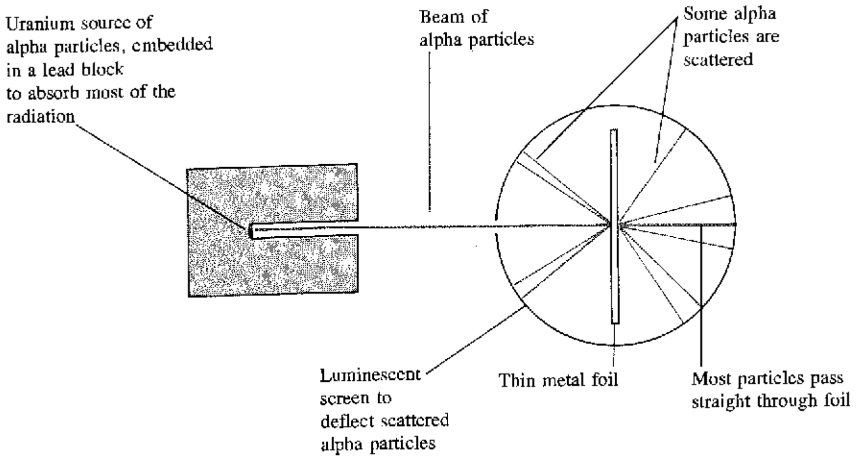

Figure 2.12

Rutherford's experiment on α-particle bombardment of metal foil.

In Rutherford's mind these results could only be explained in terms of a **nuclear atom**—an atom with a dense center of positive charge (the **nucleus**) with electrons moving around at a distance that is large relative to the nuclear radius.

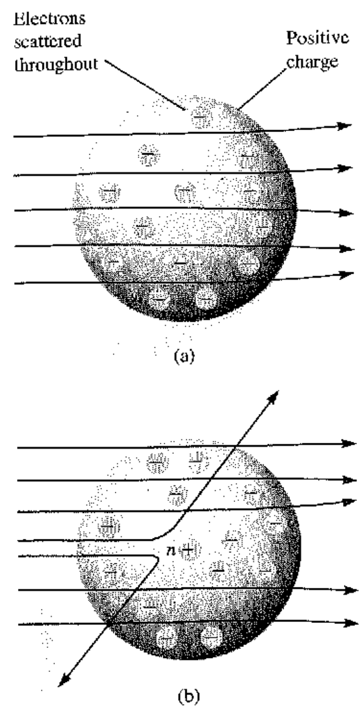

Figure 2.13

(a) The results of the metal foil experiment if Thomson's model were correct. (b) Actual results.

2.5 The Modern View of Atomic Structure—An Introduction

PURPOSE

☐ To describe features of subatomic particles.

☐ To explain the use of the symbol ^A_ZX to describe a given atom.

In the years since Thomson and Rutherford, a great deal has been learned about atomic structure. Because much of this material will be covered in detail in later chapters, only an introduction will be given here. The simplest view of the atom is that it consists of a tiny nucleus (with a radius of about 10^{-13} cm) and electrons that move about the nucleus at an average distance of about 10^{-8} cm away from it (see Fig. 2.14).

As we will see later, the chemistry of an atom mainly results from its electrons. For this reason chemists can be satisfied with a relatively crude nuclear model. The nucleus is assumed to contain **protons,** which have a positive charge equal in magnitude to the electron's negative charge, and **neutrons,** which have the same mass as a proton but no charge. The relative masses and charges of the electron, proton, and neutron are shown in Table 2.1.

Two striking things about the nucleus are its small size compared to the overall size of the atom and its extremely high density. The tiny nucleus accounts for almost all of the atom's mass. Its great density is dramatically demonstrated by the fact that a piece of nuclear material about the size of a pea would have a mass of 250 million tons!

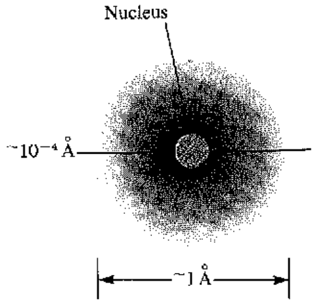

Figure 2.14

A nuclear atom viewed in cross section.

The Mass and Charge of the Electron, Proton, and Neutron		
Particle	Mass	Charge*
Electron	9.11×10^{-28} g	1 −
Proton	1.67×10^{-24} g	1 +
Neutron	1.67×10^{-24} g	none

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*The magnitude of the charge of the electron and the proton is 1.60×10^{-19} C.

Table 2.1

The *chemistry* of an atom arises from its electrons.

An important question to consider at this point is *"If all atoms are composed of these same components, why do different atoms have different chemical properties?"* The answer to this question lies in the number and arrangement of the electrons. The electrons comprise most of the atomic volume and thus are the parts that "intermingle" when atoms combine to form molecules. Therefore, the number of electrons possessed by a given atom greatly affects its ability to interact with other atoms. As a result, the atoms of different elements, which have different numbers of protons and electrons, show different chemical behavior.

A sodium atom has 11 protons in its nucleus. Since atoms have no net charge, the number of electrons must equal the number of protons. Therefore, a sodium atom has 11 electrons moving around its nucleus. It is *always* true that a sodium atom has 11 protons and 11 electrons. However, each sodium atom also has neutrons in its nucleus, and different types of sodium atoms exist that have different numbers of neutrons. For example, consider the sodium atoms represented in Fig. 2.15. These two atoms are **isotopes,** or *atoms with the same number of protons but different numbers of neutrons.* Note that the symbol for one particular type of sodium atom is written

Mass number ↘
$^{23}_{11}$Na ← Element symbol
Atomic Number ↗

where the **atomic number** Z (number of protons) is written as a subscript and the **mass number** A (the total number of protons and neutrons) is written as a superscript. (The particular atom represented here is called "sodium twenty-three." It has 11 electrons, 11 protons, and 12 neutrons.) Because the chemistry of an atom is due to its electrons, isotopes show almost identical chemical properties. In nature elements are usually found as a mixture of isotopes.

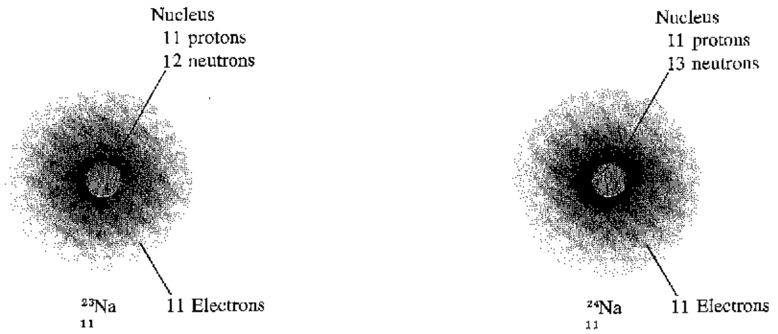


Figure 2.15

Two isotopes of sodium. Both have eleven protons and electrons, but they differ in the number of neutrons in their nuclei.

Sample Exercise 2.2

Write the symbol for the atom that has an atomic number of 9 and a mass number of 19. How many electrons and how many neutrons does this atom have?

Solution

The atomic number 9 means the atom has 9 protons. This element is called fluorine, symbolized by F. The atom is represented as

$$^{19}_{9}\text{F}$$

and is called "fluorine nineteen." Since the atom has 9 protons, it must also have 9 electrons to achieve electrical neutrality. The mass number gives the total number of protons and neutrons, which means that this atom has 10 neutrons.

2.6 Molecules and Ions

PURPOSE

☐ To introduce basic ideas of bonding in molecules.

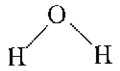
☐ To show various ways of representing molecules.

From a chemist's viewpoint the most interesting characteristic of an atom is its ability to combine with other atoms to form compounds. It was John Dalton who first recognized that chemical compounds were collections of atoms, but he could not determine the structure of atoms or their means for binding to each other. During the twentieth century we have learned that atoms have electrons and that these electrons participate in bonding one atom to another. We will discuss bonding thoroughly in Chapters 8 and 9; here we will introduce some simple bonding ideas that will be useful in the next few chapters.

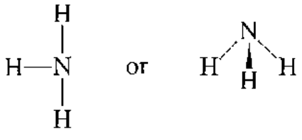
In covalent bonds atoms share electrons.

The forces that hold atoms together in compounds are called **chemical bonds.** One way that atoms can form bonds is by *sharing electrons*. These bonds are called **covalent bonds,** and the resulting collection of atoms is called a **molecule.** Molecules can be represented in several different ways. The simplest method is the **chemical formula,** in which the symbols for the elements are used to indicate the types of atoms present and subscripts are used to indicate the relative numbers of atoms. For example, the formula for carbon dioxide is CO_2, meaning that each molecule contains 1 atom of carbon and 2 atoms of oxygen.

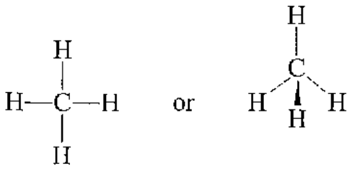
Examples of molecules that contain covalent bonds are hydrogen (H_2), water (H_2O), oxygen (O_2), ammonia (NH_3), and methane (CH_4). More information about a molecule is given by its **structural formula,** in which the individual bonds are shown (indicated by lines). Structural formulas may or may not indicate the actual shape of the molecule. For example, water might be represented as

H—O—H or 

The structure on the right shows the actual shape of the water molecule. Scientists know from experimental evidence that the molecule looks like this. (We will study the shapes of molecules further in Chapter 8.) Other examples of structural formulas are



Ammonia



Methane

In the actual structures on the right the central atom and the solid lines are understood to be in the plane of the paper. Atoms connected to the central atom by dashed lines are behind the plane of the paper, and atoms connected to the central atom by wedges are in front of the plane of the page.

In a compound composed of molecules, the individual molecules move around as independent units. For example, a sample of methane gas is represented in Fig. 2.16 using **space-filling models.** These models show the relative sizes of the atoms as well as their relative orientation in the molecule. More examples are shown in Fig. 2.17. **Ball-and-stick models** are also used to represent molecules. The ball-and-stick structure of methane is shown in Fig. 2.18.

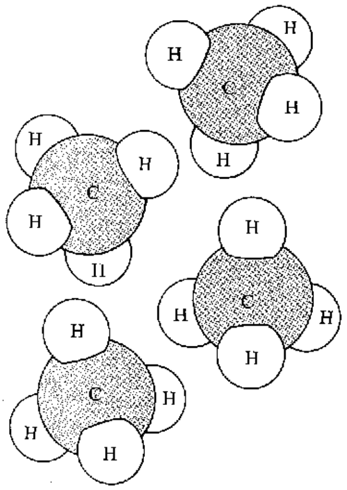


Figure 2.16

Space-filling model of methane gas. This type of model shows both the relative sizes of the atoms in the molecule and their spatial relationships.

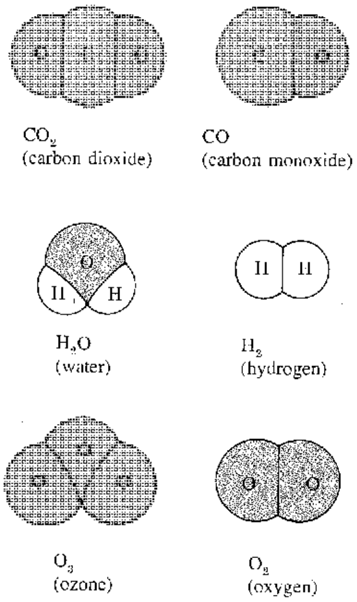


Figure 2.17

Space-filling models of various molecules.

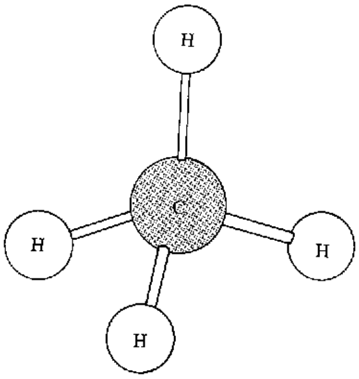
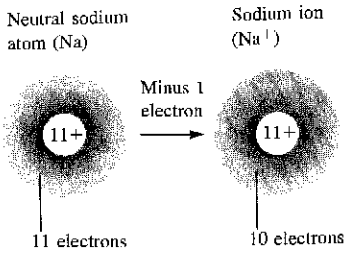


Figure 2.18

Ball-and-stick model of methane.

A second type of chemical bond results from attractions among ions. An **ion** is an atom or group of atoms that has a net positive or negative charge. The best known ionic compound is common table salt, or sodium chloride, which forms when neutral chlorine and sodium react.

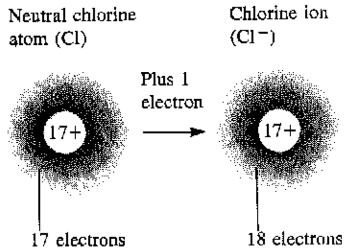
To see how ions are formed, consider what happens when an electron is transferred from sodium to chlorine (the neutrons in the nuclei will be ignored):



With one electron stripped off, the sodium, with its 11 protons and only 10 electrons, now has a net 1+ charge—it has become a *positive ion.* A positive ion is called a **cation.** The sodium ion is written as Na^+, and the process can be represented in shorthand form as

$$Na \rightarrow Na^+ + e^-$$

If an electron is added to chlorine,



the 18 electrons produce a net 1− charge; the chlorine has become an *ion with a negative charge*—an **anion.** The chloride ion is written as Cl^-, and the process is represented as

$$Cl + e^- \rightarrow Cl^-$$

Because anions and cations have opposite charges, they attract each other. This *force of attraction between oppositely charged ions* is called an **ionic bond.** Sodium metal and chlorine gas (a green gas composed of Cl_2 molecules) react to form solid sodium chloride, which contains many Na^+ and Cl^- ions packed together as shown in Fig. 2.19(a). The solid forms the beautiful colorless cubic crystals shown in Fig. 2.19(b).

A solid consisting of oppositely charged ions is called an *ionic solid,* or a *salt.* Ionic solids can consist of simple ions, as in sodium chloride, or of **polyatomic** (many-atom) **ions,** as in ammonium nitrate (NH_4NO_3), which contains ammonium cations (NH_4^+) and nitrate anions (NO_3^-). The ball-and-stick models of these ions are shown in Fig. 2.20.

CHAPTER TEN

Liquids and Solids

CONTENTS

You have only to think about water to appreciate how different the three states of matter are. Flying, swimming, and ice skating are all done in contact with water in its various forms. Clearly the arrangements of the water molecules must be significantly different in its gas, liquid, and solid forms.

In Chapter 5 we saw that a gas can be pictured as a substance whose component particles are far apart, are in rapid random motion, and exert relatively small forces on each other. The kinetic molecular model was constructed to account for the ideal behavior that most gases approach at high temperatures and low pressures.

Solids are obviously very different from gases. Gases have low density, high compressibility, and completely fill a container. Solids have much greater densities, are compressible only to a very slight extent, and are rigid—a solid maintains its shape irrespective of its container. These properties indicate that the components of a solid are close together and exert large attractive forces on each other. So a model for solids will be very different from that for gases.

The properties of liquids lie somewhere between those of solids and of gases, but not midway between, as can be seen from some of the properties of the three states of water. For example, compare the enthalpy change for the melting of ice at 0°C (the heat of fusion) to that for vaporizing liquid water at 100°C (the heat of vaporization):

$$H_2O(s) \rightarrow H_2O(l) \quad \Delta H^\circ_{fus} = 6.02 \text{ kJ/mol}$$
$$H_2O(l) \rightarrow H_2O(g) \quad \Delta H^\circ_{vap} = 41.2 \text{ kJ/mol}$$

See Section 5.6 for a discussion of the kinetic molecular theory.

CHAPTER FOURTEEN

Acids and Bases

In this chapter we reencounter two very important classes of compounds, acids and bases. We will explore their interactions and apply the fundamentals of chemical equilibria discussed in Chapter 13 to systems involving proton-transfer reactions.

Acid-base chemistry is important in a wide variety of everyday applications. There are complex systems in our bodies that carefully control the acidity of our blood, since even small deviations may lead to serious illness and death. The same sensitivity is seen in other life forms. If you have ever had tropical fish or goldfish, you know how important it is to monitor and control the acidity of the water in the aquarium.

Acids and bases are also important industrially. For example, the vast quantity of sulfuric acid manufactured in the United States each year is needed to produce fertilizers, polymers, steel, and many other materials (see the Chemical Impact in Chapter 3).

The influence of acids on living things has assumed special importance in the United States, Canada, and Europe in recent years as a result of the phenomenon of acid rain. This problem is complex and has diplomatic and economic overtones that make it all the more difficult to solve.

CONTENTS

14.1 The Nature of Acids and Bases

PURPOSE

☐ To discuss two models of acids and bases and to relate equilibrium concepts to acid dissociation.

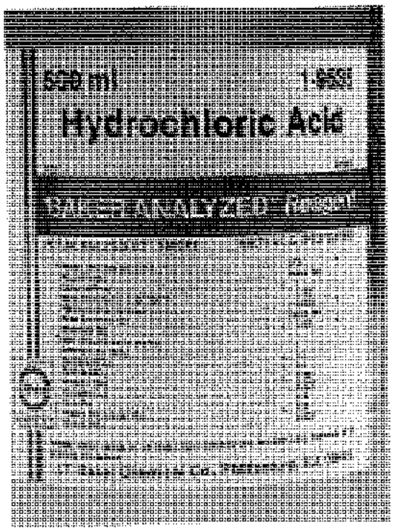
Acids were first recognized as substances that taste sour. Vinegar tastes sour because it is a dilute solution of acetic acid; citric acid is responsible for the sour taste of a lemon. Bases, sometimes called *alkalis*, are characterized by their bitter

Don't taste chemicals!

taste and slippery feel. Commercial preparations for unclogging drains are highly basic.

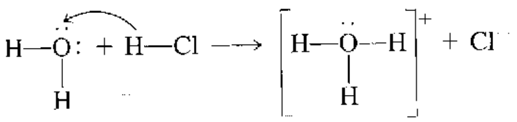
Acids and bases were first discussed in Section 4.2.

The first person to recognize the essential nature of acids and bases was Svante Arrhenius. Based on his experiments with electrolytes, Arrhenius postulated that *acids produce hydrogen ions in aqueous solution, while bases produce hydroxide ions.* At the time, the **Arrhenius concept** of acids and bases was a major step forward in quantifying acid-base chemistry, but this concept is limited because it applies only to aqueous solutions and allows for only one kind of base—the hydroxide ion. A more general definition of acids and bases was suggested by the Danish chemist Johannes Brönsted and the English chemist Thomas Lowry. In terms of the **Brönsted-Lowry model,** *an acid is a proton (H^+) donor, and a base is a proton acceptor.* For example, when gaseous HCl dissolves in water, each HCl molecule donates a proton to a water molecule, and so qualifies as a Brönsted-Lowry acid. The molecule that accepts the proton in this case, water, is a Brönsted-Lowry base.



The label on a bottle of concentrated hydrochloric acid.

To understand how water can act as a base, we need to remember that the oxygen of the water molecule has two unshared electron pairs, either of which can form a covalent bond with an H^+ ion. When gaseous HCl dissolves, the following reaction occurs:



$$H{-}\ddot{\underset{\underset{H}{|}}{O}}{:} + H{-}Cl \longrightarrow \left[H{-}\ddot{\underset{\underset{H}{|}}{O}}{-}H\right]^+ + Cl^-$$

Note that the proton is transferred from the HCl molecule to the water molecule to form H_3O^+, which is called the **hydronium ion.**

The general reaction that occurs when an acid is dissolved in water can best be represented as

Recall that (aq) means the substance is hydrated.

$$\underset{\text{Acid}}{HA(aq)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons \underset{\text{Conjugate acid}}{H_3O^+(aq)} + \underset{\text{Conjugate base}}{A^-(aq)} \tag{14.1}$$

This representation emphasizes the significant role of the polar water molecule in pulling the proton from the acid. Note that the **conjugate base** is everything that remains of the acid molecule after a proton is lost. The **conjugate acid** is formed when the proton is transferred to the base. A **conjugate acid-base pair** consists of two substances related to each other by the donating and accepting of a single proton. In Equation (14.1) there are two conjugate acid-base pairs: HA and A^-, and H_2O and H_3O^+.

It is important to note that Equation (14.1) really represents *a competition for the proton between the two bases H_2O and A^-.* If H_2O is a much stronger base than A^-, that is, if H_2O has a much greater affinity for H^+ than does A^-, the equilibrium position will be far to the right. Most of the acid dissolved will be in the ionized form. Conversely, if A^- is a much stronger base than H_2O, the equilibrium position will lie far to the left. In this case most of the acid dissolved will be present at equilibrium as HA.

The equilibrium expression for the reaction given in Equation (14.1) is

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H^+][A^-]}{[HA]} \tag{14.2}$$

where K_a is called the **acid dissociation constant.** Both $H_3O^+(aq)$ and $H^+(aq)$ are commonly used to represent the hydrated proton. In this book we will often use simply H^+, but you should remember that it is hydrated in aqueous solutions.

In Chapter 13 we saw that the concentration of a pure solid or a pure liquid is always omitted from the equilibrium expression. In a dilute solution we can assume that the concentration of liquid water remains essentially constant when an acid is dissolved. Thus the term $[H_2O]$ is not included in Equation (14.2), and the equilibrium expression for K_a has the same form as that for the simple dissociation

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

You should not forget, however, that water plays an important role in causing the acid to dissociate.

Note that K_a is the equilibrium constant for the reaction in which a proton is removed from HA to form the conjugate base A^-. We use K_a to represent *only* this type of reaction. Knowing this, you can write the K_a expression for any acid, even one that is totally unfamiliar to you. As you do Sample Exercise 14.1, focus on the definition of the reaction corresponding to K_a.

Sample Exercise 14.1

Write the simple dissociation reaction (omitting water) for each of the following acids:

- **a.** hydrochloric acid (HCl)
- **b.** acetic acid ($HC_2H_3O_2$)
- **c.** the ammonium ion (NH_4^+)
- **d.** the anilinium ion ($C_6H_5NH_3^+$)
- **e.** the hydrated aluminum(III) ion $[Al(H_2O)_6]^{3+}$

Solution

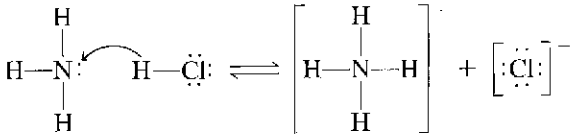
- a. $HCl(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$
- b. $HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$
- c. $NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$
- d. $C_6H_5NH_3^+(aq) \rightleftharpoons H^+(aq) + C_6H_5NH_2(aq)$
- e. Although this formula looks complicated, writing the reaction is simple if you concentrate on the meaning of K_a. Removing a proton, which can only come from one of the water molecules, leaves one OH^- and five H_2O molecules attached to the Al^{3+} ion. So the reaction is

$$[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons H^+(aq) + [Al(H_2O)_5OH]^{2+}(aq)$$

The Brönsted-Lowry model is not limited to aqueous solutions; it can be extended to reactions in the gas phase. For example, we discussed the reaction between gaseous hydrogen chloride and ammonia when we studied diffusion (Section 5.7):

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$$

In this reaction a proton is donated by the hydrogen chloride to the ammonia, as shown by these Lewis structures:



Note that this is not considered an acid-base reaction according to the Arrhenius concept.

14.2 Acid Strength

PURPOSE

☐ To relate acid strength to the position of the dissociation equilibrium.

☐ To discuss the autoionization of water.

The strength of an acid is defined by the equilibrium position of its dissociation reaction:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

A **strong acid** is one for which *this equilibrium lies far to the right*. This means that almost all the original HA is dissociated at equilibrium [see Fig. 14.1(a)]. There is an important connection between the strength of an acid and that of its conjugate base. *A strong acid yields a weak conjugate base*—one that has a low affinity for a proton. A strong acid can also be described as an acid whose conjugate base is a much weaker base than water (see Fig. 14.2). In this case the water molecules win the competition for the H^+ ions.

A strong acid has a weak conjugate base.

Conversely, a **weak acid** is one for which *the equilibrium lies far to the left*. Most of the acid originally placed in the solution is still present as HA at equilibrium. That is, a weak acid dissociates only to a very small extent in aqueous solution [see Fig. 14.1(b)]. In contrast to a strong acid, a weak acid has a conjugate base

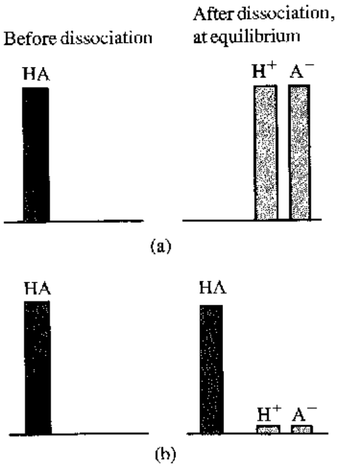


Figure 14.1

Graphical representation of the behavior of acids of different strengths in aqueous solution. (a) A strong acid is completely dissociated. (b) In contrast, only a small fraction of the molecules of a weak acid are dissociated at equilibrium.

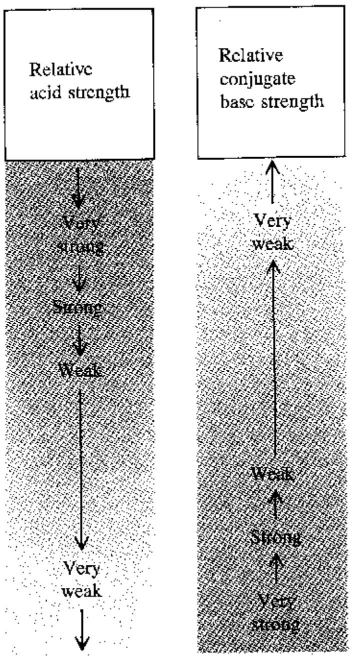


Figure 14.2

The relationship of acid strength and conjugate base strength for the dissociation reaction

$$\underset{\text{Acid}}{HA(aq)} + H_2O(l) \rightleftharpoons H_3O^+(aq) + \underset{\text{Conjugate base}}{A^-(aq)}$$

that is a much stronger base than water. In this case a water molecule is not very successful in pulling an H^- ion from the conjugate base. *A weak acid yields a relatively strong conjugate base.*

The various ways of describing the strength of an acid are summarized in Table 14.1.

Various Ways to Describe Acid Strength		
Property	Strong acid	Weak acid
K_a value	K_a is large	K_a is small
Position of the dissociation equilibrium	Far to the right	Far to the left
Equilibrium concentration of H^+ compared to original concentration of HA	$[H^-] \approx [HA]_0$	$[H^-] \ll [HA]_0$
Strength of conjugate base compared to that of water	A^- much weaker base than H_2O	A^- much stronger base than H_2O

Table 14.1

$\ll$ means much less than
$\gg$ means much greater than

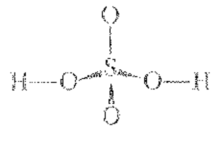
The common strong acids are sulfuric acid ($H_2SO_4(aq)$), hydrochloric acid ($HCl(aq)$), nitric acid ($HNO_3)(aq)$, and perchloric acid ($HClO_4(aq)$). Sulfuric acid is actually a **diprotic acid,** an acid having two acidic protons. The acid H_2SO_4 is a strong acid, virtually 100% dissociated in water:

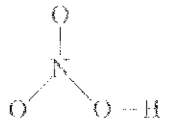
$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$$

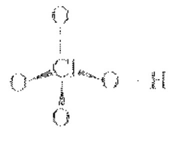
but the HSO_4^- ion is a weak acid:

$$HSO_4^-(aq) \rightleftharpoons H^-(aq) + SO_4^{2-}(aq)$$

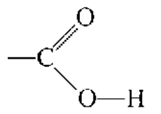
Perchloric acid can explode if handled improperly.


Sulfuric acid


Nitric acid


Perchloric acid

Most acids are **oxyacids,** in which the acidic proton is attached to an oxygen atom. The strong acids mentioned above, except hydrochloric acid, are typical examples. Many common weak acids, such as phosphoric acid (H_3PO_4), nitrous acid (HNO_2), and hypochlorous acid (HOCl), are also oxyacids. **Organic acids,** those with a carbon-atom backbone, commonly contain the **carboxyl group:**

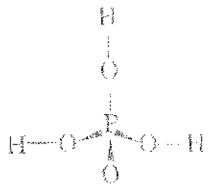


Acids of this type are usually weak. Examples are acetic acid (CH_3COOH), often written $HC_2H_3O_2$, and benzoic acid (C_6H_5COOH).

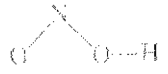
There are some important acids in which the acidic proton is attached to an atom other than oxygen. The most significant of these are the hydrohalic acids *HX*, where *X* represents a halogen atom.

Table 14.2 contains a list of common **monoprotic acids** (those having *one* acidic proton) and their K_a values. Note that the strong acids are not listed. When a strong acid molecule such as HCl, for example, is placed in water, the position of the dissociation equilibrium

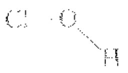
$$HCl(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$$



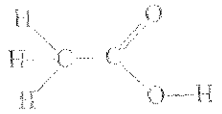
Phosphoric acid



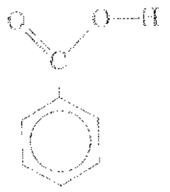
Nitrous acid



Hypochlorous acid



Acetic acid



Benzoic acid

Values of K_a for Some Common Monoprotic Acids

Formula	Name	Value of K_a*
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
$HC_2H_2ClO_2$	Monochloracetic acid	1.35×10^{-3}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
$HC_2H_3O_2$	Acetic acid	1.8×10^{-5}
$[Al(H_2O)_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}
$HOCl$	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HOC_6H_5	Phenol	1.6×10^{-10}

↑ Increasing acid strength

---

*The units of K_a are mol/L, but are customarily omitted.

Table 14.2

lies so far to the right that [HCl] cannot be measured accurately. This prevents an accurate calculation of K_a:

$$K_a = \frac{[H^+][Cl^-]}{\underset{\nwarrow\text{Very small and highly uncertain}}{[HCl]}}$$

Sample Exercise 14.2

Using Table 14.2, arrange the following species according to their strength as bases: H_2O, F^-, Cl^-, NO_2^-, CN^-.

Solution

Remember that water is a stronger base than the conjugate base of a strong acid, but a weaker base than the conjugate base of a weak acid. This leads to the following order:

$$Cl^- < H_2O < \text{conjugate bases of weak acids}$$

Weakest bases ⟶ Strongest bases

We can order the remaining conjugate bases by recognizing that the strength of an acid is *inversely related* to the strength of its conjugate base. Since from Table 14.2 we have

$$K_a \text{ for HF} > K_a \text{ for } HNO_2 > K_a \text{ for HCN}$$

the base strengths increase as follows:

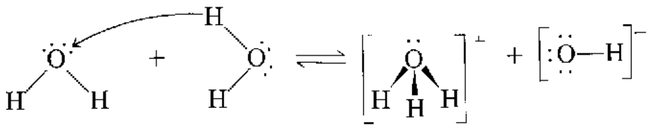
$$F^- < NO_2^- < CN^-$$

The combined order of increasing base strength is

$$Cl^- < H_2O < F^- < NO_2^- < CN^-$$

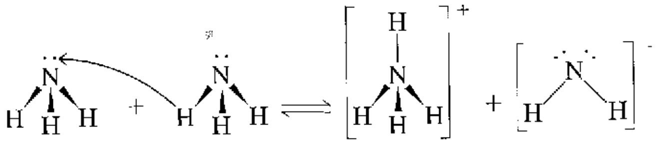
Water as an Acid and a Base

A substance is said to be *amphoteric* if it can behave either as an acid or as a base. Water is the most common **amphoteric substance.** We can see this clearly in the **autoionization** of water, which involves the transfer of a proton from one water molecule to another to produce a hydroxide ion and a hydronium ion:



In this reaction one water molecule acts as an acid by furnishing a proton, and the other acts as a base by accepting the proton.

Autoionization can occur in other liquids besides water. For example, in liquid ammonia the autoionization reaction is



The autoionization reaction for water

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

leads to the equilibrium expression

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-]$$

where K_w, called the **ion-product constant** (or the *dissociation constant*), always refers to the autoionization of water.

Experiment shows that at 25°C

$$[H^+] = [OH^-] = 1.0 \times 10^{-7}\ M$$

which means that at 25°C

$$\begin{aligned} K_w &= [H^+][OH^-] = (1.0 \times 10^{-7}\ \text{mol/L})(1.0 \times 10^{-7}\ \text{mol/L}) \\ &= 1.0 \times 10^{-14}\ \text{mol}^2/\text{L}^2 \end{aligned}$$

$K_w = [H^+][OH^-]$
$= 1.0 \times 10^{-14}$

The units are customarily omitted.

It is important to recognize the meaning of K_w. In any aqueous solution at 25°C, *no matter what it contains,* the product of $[H^+]$ and $[OH^-]$ must always equal 1.0×10^{-14}. There are three possible situations:

1. A neutral solution, where $[H^+] = [OH^-]$.
2. An acidic solution, where $[H^+] > [OH^-]$.
3. A basic solution, where $[OH^-] > [H^+]$.

In each case, however, at 25°C

$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$

Sample Exercise 14.3

Calculate $[H^+]$ or $[OH^-]$ as required for each of the following solutions at 25°C, and state whether the solution is neutral, acidic, or basic.

a. $1.0 \times 10^{-5}\ M\ OH^-$

Solution

$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$. Since $[OH^-]$ is $1.0 \times 10^{-5}\ M$, solving for $[H^+]$ gives

$$[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} = 1.0 \times 10^{-9}\ M$$

Since $[OH^-] > [H^+]$, the solution is basic.

b. $1.0 \times 10^{-7}\ M\ OH^-$.

Solution

As in part a, solving for $[H^+]$ gives

$$[H^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7}\ M$$

Since $[H^+] = [OH^-]$, the solution is neutral.

c. $10.0\ M\ H^+$.

Solution

Solving for $[OH^-]$ gives

$$[OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]} = \frac{1.0 \times 10^{-14}}{10.0} = 1.0 \times 10^{-15}\ M$$

Since $[H^+] > [OH^-]$, the solution is acidic.

Since K_w is an equilibrium constant, it varies with temperature. The effect of temperature is considered in Sample Exercise 14.4.

Sample Exercise 14.4

At 60°C the value of K_w is 1×10^{-13}.

a. Using Le Châtelier's principle, predict whether the reaction

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

is exothermic or endothermic.

b. Calculate $[H^+]$ and $[OH^-]$ in a neutral solution at 60°C.

Solution

a. K_w *increases* from 1×10^{-14} at 25°C to 1×10^{-13} at 60°C. Le Châtelier's principle states that if a system at equilibrium is heated, it will adjust to consume energy. Since the value of K_w increases with temperature, we must think of energy as a reactant, and so the process must be endothermic.

b. At 60°C

$$[H^+][OH^-] = 1 \times 10^{-13}$$

For a neutral solution

$$[H^+] = [OH^-] = \sqrt{1 \times 10^{-13}} = 3 \times 10^{-7}\ M$$

14.3 The pH Scale

PURPOSE

☐ To define pH, pOH, and pK and to introduce general methods for solving acid-base problems.

Because $[H^+]$ in an aqueous solution is typically quite small, the **pH scale** provides a convenient way to represent solution acidity. The pH is a log scale based on 10 where

The pH scale is a compact way to represent solution acidity.

$$\text{pH} = -\log[H^+]$$

Thus for a solution where

$$[H^+] = 1.0 \times 10^{-7}\ M$$
$$\text{pH} = -(-7.00) = 7.00$$

At this point we need to discuss significant figures for logarithms. The rule is that *the number of decimal places in the log is equal to the number of significant figures in the original number*. Thus

Appendix 1.2 has a review of logs.

$$[H^+] = \overset{\swarrow\text{2 significant figures}}{1.0} \times 10^{-9}\ M$$
$$\text{pH} = \underset{\nwarrow\text{2 decimal places}}{9.00}$$

Similar log scales are used for representing other quantities, for example:

$$\text{pOH} = -\log[OH^-]$$
$$\text{p}K = -\log K$$

Since pH is a log scale based on 10, *the pH changes by 1 for every power of 10 change in $[H^+]$*. For example, a solution of pH 3 has an H^+ concentration 10 times that of a solution of pH 4 and 100 times that of a solution of pH 5. Also note that because pH is defined as $-\log[H^+]$, *the pH decreases as $[H^+]$ increases*. The pH scale and the pH values for several common substances are shown in Fig. 14.3.

For $\Delta[H^+] = 10$, $\Delta\text{pH} = 1$.

The pH decreases as $[H^+]$ increases, and vice versa.

The pH of a solution is usually measured using a pH meter, an electronic device with a probe that can be inserted into a solution of unknown pH. The probe contains an acidic aqueous solution enclosed by a special glass membrane that allows migration of H^+ ions. If the unknown solution has a different pH from the solution in the probe, an electrical potential results, which is registered on the meter (see Fig. 14.4).

The pH meter is discussed more fully in Section 17.4.

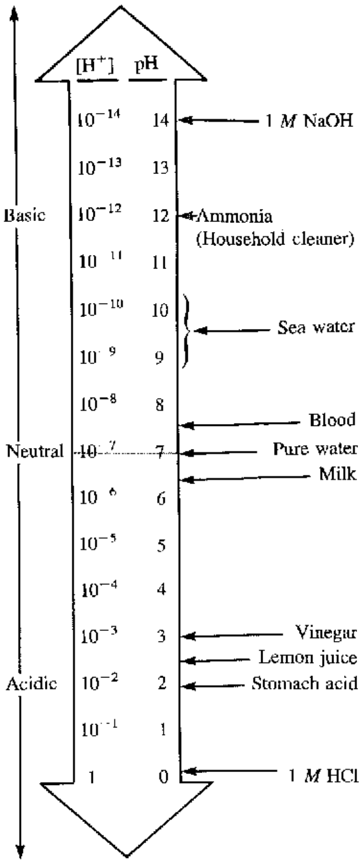


Figure 14.3

The pH scale and pH values of some common substances.

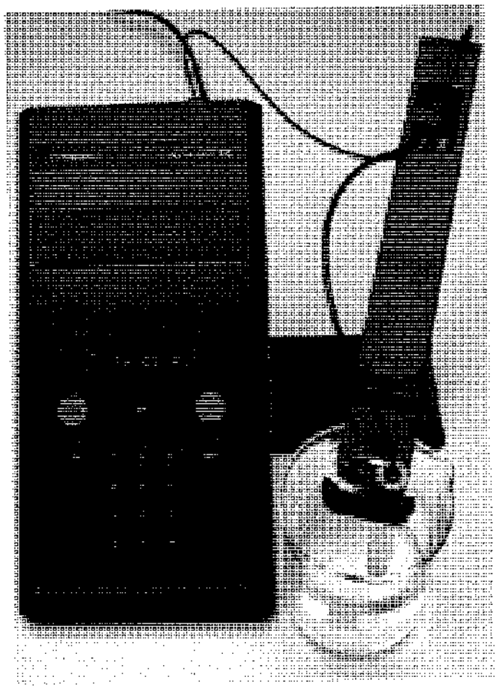


Figure 14.4

A typical pH meter. The probe at the right is placed in the solution with unknown pH. The difference between the $[H^+]$ in the solution sealed into the probe and the $[H^+]$ in the solution being analyzed is translated into an electrical potential and registered on the meter as a pH reading.

Sample Exercise 14.5

Calculate pH and pOH for each of the following solutions at 25°C:

a. $1.0 \times 10^{-3}\ M\ OH^-$ **b.** $1.0\ M\ H^+$.

Solution

a.

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11}\ M$$

$$pH = -\log[H^+] = -\log(1.0 \times 10^{-11}) = 11.00$$

$$pOH = -\log[OH^-] = -\log(1.0 \times 10^{-3}) = 3.00$$

b.

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0} = 1.0 \times 10^{-14}\ M$$

$$pH = -\log[H^+] = -\log(1.0) = 0$$

$$pOH = -\log[OH^-] = -\log(1.0 \times 10^{-14}) = 14.00$$

It is useful to consider the log form of the expression

$$K_w = [H^+][OH^-]$$

That is,

$$\log K_w = \log[H^+] + \log[OH^-]$$

or

$$-\log K_w = -\log[H^+] - \log[OH^-]$$

Thus

$$pK_w = pH + pOH \qquad (14.3)$$

Since $K_w = 1.0 \times 10^{-14}$,

$$pK_w = -\log(1.0 \times 10^{-14}) = 14.00$$

Thus, for *any* aqueous solution at 25°C, pH and pOH add up to 14.00.

$$\text{pH} + \text{pOH} = 14.00 \qquad (14.4)$$

Sample Exercise 14.6

The pH of a sample of human blood was measured to be 7.41 at 25°C. Calculate pOH, $[H^+]$, and $[OH^-]$ for the sample.

Solution

Since pH + pOH = 14.00,

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 7.41 = 6.59$$

To find $[H^+]$ we must go back to the definition of pH:

$$\text{pH} = -\log[H^+]$$

Thus $$7.41 = -\log[H^+] \quad \text{or} \quad \log[H^+] = -7.41$$

We need to know the *antilog* of −7.41. As shown in Appendix 1.2, taking the antilog is the same as exponentiation, that is,

$$\text{antilog}(n) = 10^n$$

There are different methods for carrying out the antilog operation on various calculators. The most common are the $\boxed{10^x}$ key and the two-key $\boxed{\text{INV}}$ $\boxed{\text{LOG}}$ sequence. Consult the user's manual for your calculator to find out how to do the antilog operation.

Since $\text{pH} = -\log[H^+]$,

$$-\text{pH} = \log[H^+]$$

and $[H^+]$ can be calculated by taking the antilog of −pH:

$$[H^+] = \text{antilog}(-\text{pH})$$

In the present case

$$[H^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-7.41) = 10^{-7.41} = 3.9 \times 10^{-8}$$

Similarly, $[OH^-] = \text{antilog}(-\text{pOH})$, and

$$[OH^-] = \text{antilog}(-6.59) = 10^{-6.59} = 2.6 \times 10^{-7}\ M$$

Now that we have considered all of the fundamental definitions relevant to acid-base solutions, we can proceed to a quantitative description of the equilibria present in these solutions. The main reason that acid-base problems seem difficult is that a typical aqueous solution contains many components so the problems tend to be complicated. However, you can deal with these problems successfully if you use the following general strategies:

- *Think chemistry.* Focus on the solution components and their reactions. It will almost always be possible to choose one reaction that is the most important.

- *Be systematic*. Acid-base problems require a step-by-step approach.
- *Be flexible*. Although all acid-base problems are similar in many ways, important differences do occur. Treat each problem as a separate entity. Do not try to force a given problem into matching any you have solved before. Look for both the similarities and the differences.
- *Be patient*. The complete solution to a complicated problem cannot be seen immediately in all its detail. Pick the problem apart into its workable steps.
- *Be confident*. Look within the problem for the solution, and let the problem guide you. Assume that you can think it out. Do not rely on memorizing solutions to problems. In fact, memorizing solutions is usually detrimental because you tend to try to force a new problem to be the same as one you have seen before. *Understand and think; don't just memorize.*

14.4 Calculating the pH of Strong Acid Solutions

PURPOSE

☐ To demonstrate the systematic treatment of solutions of strong acids.

When we deal with acid-base equilibria, *it is essential to focus on the solution components and their chemistry*. For example, what species are present in a 1.0 *M* solution of HCl? Since hydrochloric acid is a strong acid, we assume that it is completely dissociated. Thus, although the label on the bottle says 1.0 *M* HCl, the solution contains virtually no HCl molecules. Typically, container labels indicate the substance(s) used to make up the solution, but do not necessarily describe the solution components after dissolution. Thus a 1.0 *M* HCl solution contains H^+ and Cl^- ions rather than HCl molecules.

The next step in dealing with aqueous solutions is to determine which components are significant and which can be ignored. We need to focus on the **major species,** those solution components present in relatively large amounts. In 1.0 *M* HCl, for example, the major species are H^+, Cl^-, and H_2O. Since this is a very acidic solution, OH^- is present only in tiny amounts and is classed as a minor species. In attacking acid-base problems, the importance of *writing the major species in the solution* as the first step cannot be overemphasized. *This single step is the key to solving these problems successfully.*

Always write the major species present in the solution.

To illustrate the main ideas involved, let us calculate the pH of 1.0 *M* HCl. We first list the major species: H^+, Cl^-, and H_2O. Since we want to calculate the pH, we will focus on those major species that can furnish H^+. Obviously, we must consider H^+ from the dissociation of HCl. However, H_2O also furnishes H^+ by autoionization, which is often represented by the simple dissociation reaction

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

But is autoionization an important source of H^+ ions? In pure water at 25°C, $[H^+]$ is 10^{-7} *M*. In 1.0 *M* HCl solution, the water will produce even less than 10^{-7} *M* H^+, since by Le Châtelier's principle, the H^+ from the dissociated HCl will drive the position of the water equilibrium to the left. Thus the amount of H^+ contributed by water is negligible compared to the 1.0 *M* H^+ from the dissociation of HCl. There-

The H^+ from the strong acid drives the equilibrium $H_2O \rightleftharpoons H^+ + OH^-$ to the left.

fore, we can say that $[H^+]$ in the solution is 1.0 *M*. The pH is then

$$pH = -\log[H^+] = -\log(1.0) = 0$$

Sample Exercise 14.7

a. Calculate the pH of 0.10 *M* HNO_3.

Solution

a. Since HNO_3 is a strong acid, the major species in solution are:

$$H^+, NO_3^-, \text{ and } H_2O$$

The concentration of HNO_3 is virtually zero, since the acid completely dissociates in water. Also, $[OH^-]$ will be very small because the H^+ ions from the acid will drive the equilibrium

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

to the left. That is, this is an acidic solution where $[H^+] \gg [OH^-]$ and so $[OH^-] \ll 10^{-7}$ *M*. The sources of H^+ are

1. H^+ from HNO_3 (0.10 *M*).
2. H^+ from H_2O

The number of H^+ ions contributed by the autoionization of water will be very small compared to the 0.10 *M* contributed by the HNO_3 and can be neglected. Since the dissolved HNO_3 is the only important source of H^+ ions in this solution,

$$[H^+] = 0.10\ M \quad \text{and} \quad pH = -\log(0.10) = 1.00$$

b. Calculate the pH of 1.0×10^{-10} *M* HCl.

Solution

Normally, in an aqueous solution of HCl the major species are H^+, Cl^-, and H_2O. However, in this case the amount of HCl in solution is so small that it has no effect; the only major species is H_2O. Thus the pH will be that of pure water, or pH = 7.00.

14.5 Calculating the pH of Weak Acid Solutions

PURPOSE

- To demonstrate the systematic treatment of solutions of weak acids.
- To show how to calculate percent dissociation.

Since a weak acid dissolved in water can be viewed as a prototype of almost any equilibrium occurring in aqueous solution, we will proceed carefully and systematically. Although some of the procedures we develop here may seem superfluous, they will become essential as the problems become more complicated. We will develop the necessary strategies by calculating the pH of a 1.00 *M* solution of HF ($K_a = 7.2 \times 10^{-4}$).

First, always write the major species present in the solution.

The first step, as always, is to *write the major species in the solution*. From its small K_a value, we know that hydrofluoric acid is a weak acid and will be dissociated only to a slight extent. Thus, when we write the major species, the hydrofluoric acid will be represented in its dominant form, as HF. The major species in solution are: HF and H_2O.

The next step (since this is a pH problem) is to decide which of the major species can furnish H^+ ions. Actually, both major species can do so:

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \qquad K_a = 7.2 \times 10^{-4}$$
$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.0 \times 10^{-14}$$

But in aqueous solutions typically one source of H^+ can be singled out as dominant. By comparing K_a for HF to K_w for H_2O, we see that hydrofluoric acid, although weak, is still a much stronger acid than water. Thus we will assume that hydrofluoric acid will be the dominant source of H^+. We will ignore the tiny contribution by water.

Therefore, it is the dissociation of HF that will determine the equilibrium concentration of H^+ and hence the pH:

$$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$$

The equilibrium expression is

$$K_a = 7.2 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]}$$

To solve the equilibrium problem, we follow the procedures developed in Chapter 13 for gas-phase equilibria. First, we list the initial concentrations, the *concentrations before the reaction of interest has proceeded to equilibrium*. Before any HF dissociates, the concentrations of the species in the equilibrium are:

$$[HF]_0 = 1.00\ M \qquad [F^-]_0 = 0 \qquad [H^+]_0 = 10^{-7}\ M \approx 0$$

(Note that the zero value for $[H^+]_0$ is an approximation, since we are neglecting the H^+ ions from the autoionization of water.)

The next step is to determine the change required to reach equilibrium. Since some HF will dissociate to come to equilibrium (but that amount is presently unknown), we let x be the change in the concentration of HF that is required to achieve equilibrium. That is, we assume that x mol/L of HF will dissociate to produce x mol/L H^+ and x mol/L F^- as the system adjusts to its equilibrium position. Now the equilibrium concentrations can be defined in terms of x:

$$[HF] = [HF]_0 - x = 1.00 - x$$
$$[F^-] = [F^-]_0 + x = 0 + x = x$$
$$[H^+] = [H^+]_0 + x \approx 0 + x = x$$

Substituting these equilibrium concentrations into the equilibrium expression gives

$$K_a = 7.2 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]} = \frac{(x)(x)}{1.00 - x}$$

This expression produces a quadratic equation that can be solved using the quadratic formula, as for the gas-phase systems in Chapter 13. However, since K_a for HF is so small, HF will dissociate only slightly, and x is expected to be small. This will allow us to simplify the calculation. If x is very small compared to 1.00, the term in the denominator can be approximated as follows:

$$1.00 - x \approx 1.00$$

The equilibrium expression then becomes

$$7.2 \times 10^{-4} = \frac{(x)(x)}{1.00 - x} \approx \frac{(x)(x)}{1.00}$$

which yields

$$x^2 \approx (7.2 \times 10^{-4})(1.00) = 7.2 \times 10^{-4}$$
$$x \approx \sqrt{7.2 \times 10^{-4}} = 2.7 \times 10^{-2}$$

How valid is the approximation that [HF] = 1.00 M? Because this question will arise often in connection with acid-base equilibrium calculations, we will consider it carefully. *The validity of the approximation depends on how much accuracy we demand for the calculated value of [H^+].* Typically, the K_a values for acids are known to an accuracy of only about ±5%. It is reasonable therefore to apply this figure when determining the validity of the approximation

The validity of an approximation should always be checked.

$$[HA]_0 - x \approx [HA]_0$$

We will use the following test.

We first calculate the value of x by making the following approximation

$$K_a = \frac{x^2}{[HA]_0 - x} \approx \frac{x^2}{[HA]_0}$$

where

$$x^2 \approx K_a[HA]_0 \quad \text{and} \quad x \approx \sqrt{K_a[HA]_0}$$

We then compare the sizes of x and $[HA]_0$. If the expression

$$\frac{x}{[HA]_0} \times 100$$

is less than or equal to 5%, the value of x is so small that the approximation

$$[HA]_0 - x \approx [HA]_0$$

will be considered valid.

In our example

$$x = 2.7 \times 10^{-2} \text{ mol/L}$$
$$[HA]_0 = [HF]_0 = 1.00 \text{ mol/L}$$

and

$$\frac{x}{[HA]_0} \times 100 = \frac{2.7 \times 10^{-2}}{1.00} \times 100 = 2.7\%$$

The approximation we made is considered valid, and the value of x calculated using that approximation is acceptable. Thus

$$x = [H^+] = 2.7 \times 10^{-2}\ M \quad \text{and} \quad pH = -\log(2.7 \times 10^{-2}) = 1.57$$

This problem illustrates all the important steps for solving a typical equilibrium problem involving a weak acid. These steps are summarized as follows:

Solving Weak Acid Equilibrium Problems

- List the major species in the solution.
- Choose the species that can produce H^+, and write balanced equations for the reactions producing H^+.
- Using the values of the equilibrium constants for the reactions you have written, decide which equilibrium will dominate in producing H^+.
- Write the equilibrium expression for the dominant equilibrium.
- List the initial concentrations of the species participating in the dominant equilibrium.
- Define the change needed to achieve equilibrium; that is, define x.
- Write the equilibrium concentrations in terms of x.
- Substitute the equilibrium concentrations into the equilibrium expression.
- Solve for x the "easy" way; that is, by assuming that $[HA]_0 - x \approx [HA]_0$.
- Use the 5% rule to verify whether the approximation is valid.
- Calculate $[H^+]$ and pH.

We use this systematic approach in Sample Exercise 14.8.

Sample Exercise 14.8

The hypochlorite ion (OCl^-) is a strong oxidizing agent often found in household bleaches and disinfectants. It is also the active ingredient that forms when swimming pool water is treated with chlorine. In addition to its oxidizing abilities, the hypochlorite ion has a relatively high affinity for protons (it is a much stronger base than Cl^-, for example) and forms the weakly acidic hypochlorous acid ($HOCl$, $K_a = 3.5 \times 10^{-8}$). Calculate the pH of a 0.100 *M* aqueous solution of hypochlorous acid.

Solution

STEP 1
We list the major species. Since HOCl is a weak acid and remains mostly undissociated, the major species in a 0.100 *M* HOCl solution are

$$HOCl \quad \text{and} \quad H_2O$$

STEP 2
Both species can produce H^+:

$$HOCl(aq) \rightleftharpoons H^+(aq) + OCl^-(aq) \qquad K_a = 3.5 \times 10^{-8}$$
$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.0 \times 10^{-14}$$

STEP 3
Since HOCl is a significantly stronger acid than H_2O, it will dominate in the production of H^+.

STEP 4

We therefore use the following equilibrium expression:

$$K_a = 3.5 \times 10^{-8} = \frac{[H^+][OCl^-]}{[HOCl]}$$

STEP 5

The initial concentrations appropriate for this equilibrium are

$$[HOCl]_0 = 0.100\ M$$
$$[OCl^-]_0 = 0$$
$$[H^+]_0 \approx 0 \qquad \text{(We neglect the contribution from } H_2O\text{.)}$$

STEP 6

Since the system will reach equilibrium by the dissociation of HOCl, let x be the amount of HOCl (in mol/L) that dissociates in reaching equilibrium.

STEP 7

The equilibrium concentrations in terms of x are

$$[HOCl] = [HOCl]_0 - x = 0.100 - x$$
$$[OCl^-] = [OCl^-]_0 + x = 0 + x = x$$
$$[H^+] = [H^+]_0 + x \approx 0 + x = x$$

STEP 8

Substituting these concentrations into the equilibrium expression gives

$$K_a = 3.5 \times 10^{-8} = \frac{(x)(x)}{0.100 - x}$$

STEP 9

Since K_a is so small, we can expect a small value for x. Thus we make the approximation $[HA]_0 - x \approx [HA]_0$, or $0.100 - x \approx 0.100$, which leads to the expression

$$K_a = 3.5 \times 10^{-8} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

Solving for x gives

$$x = 5.9 \times 10^{-5}$$

STEP 10

The approximation $0.100 - x \approx 0.100$ must be validated. To do this, we compare x to $[HOCl]_0$:

$$\frac{x}{[HA]_0} \times 100 = \frac{x}{[HOCl]_0} \times 100 = \frac{5.9 \times 10^{-5}}{0.100} \times 100 = 0.059\%$$

Since this value is much less than 5%, the approximation is considered valid.

STEP 11

We calculate $[H^+]$ and pH:

$$[H^+] = x = 5.9 \times 10^{-5}\ M \quad \text{and} \quad \text{pH} = 4.23$$

The pH of a Mixture of Weak Acids

The same systematic approach applies to all solution equilibria.

Sometimes a solution contains two weak acids of very different strengths. This case is considered in Sample Exercise 14.9. Note that the steps are again followed (though not labeled).

Sample Exercise 14.9

Calculate the pH of a solution that contains 1.00 M HCN ($K_a = 6.2 \times 10^{-10}$) and 5.00 M HNO_2 ($K_a = 4.0 \times 10^{-4}$). Also calculate the concentration of cyanide ion (CN^-) in this solution at equilibrium.

Solution

Since HCN and HNO_2 are both weak acids and are largely undissociated, the major species in the solution are:

$$HCN, \quad HNO_2, \quad \text{and} \quad H_2O.$$

All three of these components produce H^+.

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq) \qquad K_a = 6.2 \times 10^{-10}$$
$$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq) \qquad K_a = 4.0 \times 10^{-4}$$
$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.0 \times 10^{-14}$$

A mixture of three acids might lead to a very complicated problem. However, the situation is greatly simplified by the fact that, even though HNO_2 is a weak acid, it is much stronger than the other two acids present (as revealed by the K values). Thus HNO_2 can be assumed to be the dominant producer of H^+, and we will focus on the equilibrium expression:

$$K_a = 4.0 \times 10^{-4} = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

The initial concentrations, the definition of x, and the equilibrium concentrations are as follows:

Initial concentration (mol/L)		Equilibrium concentration (mol/L)
$[HNO_2]_0 = 5.00$	$\xrightarrow{x \text{ mol/L } HNO_2}$ dissociates	$[HNO_2] = 5.00 - x$
$[NO_2^-]_0 = 0$		$[NO_2^-] = x$
$[H^+]_0 \approx 0$		$[H^+] \approx x$

Substituting the equilibrium concentrations in the equilibrium expression and making the approximation that $5.00 - x = 5.00$, gives

$$K_a = 4.0 \times 10^{-4} = \frac{(x)(x)}{5.00 - x} \approx \frac{x^2}{5.00}$$

We solve for x:

$$x = 4.5 \times 10^{-2}$$

Using the 5% rule, we show that the approximation is valid:

$$\frac{x}{[HNO_2]_0} \times 100 = \frac{4.5 \times 10^{-2}}{5.00} \times 100 = 0.90\%$$

Therefore

$$[H^+] = x = 4.5 \times 10^{-2}\ M \quad \text{and} \quad pH = 1.35$$

We also want to calculate the equilibrium concentration of cyanide ion in this solution. The CN^- ions in this solution come from the dissociation of HCN:

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$$

Although the position of this equilibrium lies far to the left and does not contribute *significantly* to $[H^+]$, HCN is the *only source* of CN^-. Thus we must consider the extent of the dissociation of HCN to calculate $[CN^-]$. The equilibrium expression for the above reaction is

$$K_a = 6.2 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]}$$

In equilibrium problems, no distinction is made as to the sources of a given species.

We know $[H^+]$ for this solution from the results for the first part of the problem. It is important to understand that *there is only one kind of* H^+ *in this solution*. It does not matter from which acid the H^+ ions originate. The equilibrium value of $[H^+]$ for the HCN dissociation is $4.5 \times 10^{-2}\ M$, even though the H^+ was contributed almost entirely from dissociation of HNO_2. What is [HCN] at equilibrium? We know $[HCN]_0 = 1.00\ M$, and since K_a for HCN is so small, a negligible amount of HCN will dissociate. Thus

$$[HCN] = [HCN]_0 - \text{amount of HCN dissociated} \approx [HCN]_0 = 1.00\ M$$

Since $[H^+]$ and [HCN] are known, we can find $[CN^-]$ from the equilibrium expression:

$$K_a = 6.2 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]} = \frac{(4.5 \times 10^{-2})[CN^-]}{1.00}$$

$$[CN^-] = \frac{(6.2 \times 10^{-10})(1.00)}{4.5 \times 10^{-2}} = 1.4 \times 10^{-8}\ M$$

Note the significance of this result. Since $[CN^-] = 1.4 \times 10^{-8}\ M$, and HCN is the only source of CN^-, this means that only 1.4×10^{-8} mol/L of HCN has dissociated. This is a very small amount compared to the initial concentration of HCN, which is exactly what we would expect from its very small K_a value, and $[HCN] = 1.00\ M$ as assumed.

Percent Dissociation

It is often useful to specify the amount of weak acid that has dissociated in achieving equilibrium in an aqueous solution. The **percent dissociation** is defined as follows:

$$\text{Percent dissociation} = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \times 100 \qquad (14.5)$$

For example, we found earlier that in a 1.00 M solution of HF, $[H^+] = 2.7 \times 10^{-2}\ M$. To reach equilibrium, 2.7×10^{-2} mol/L of the original 1.00 M HF dissociates, so

$$\text{Percent dissociation} = \frac{2.7 \times 10^{-2}\ \text{mol/L}}{1.00\ \text{mol/L}} \times 100 = 2.7\%$$

For a given weak acid, the percent dissociation increases as the acid becomes more dilute. For example, the percent dissociation of acetic acid ($HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$) is significantly greater in a 0.10 M solution than in a 1.0 M solution, as is demonstrated in Sample Exercise 14.10.

Sample Exercise 14.10

Calculate the percent dissociation of acetic acid ($K_a = 1.8 \times 10^{-5}$) in each of the following solutions:

a. 1.00 M $HC_2H_3O_2$

b. 0.100 M $HC_2H_3O_2$

Solution

a. Since acetic acid is a weak acid, the major species in this solution are $HC_2H_3O_2$ and H_2O. Both species are weak acids, but acetic acid is much stronger than water. Thus the dominant equilibrium will be

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

and the equilibrium expression is

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

The initial concentrations, definition of x, and the equilibrium concentrations are as follows:

Initial concentration (mol/L)		Equilibrium concentration (mol/L)
$[HC_2H_3O_2]_0 = 1.00\ M$ $[C_2H_3O_2^-]_0 = 0$ $[H^+]_0 \approx 0$	$\xrightarrow[\text{dissociates}]{x\ \text{mol/L}\ HC_2H_3O_2}$	$[HC_2H_3O_2] = 1.00 - x$ $[C_2H_3O_2^-] = x$ $[H^+] = x$

Inserting the equilibrium concentrations into the equilibrium expression and making the usual approximation that x is small compared to $[HA]_0$, gives

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(x)(x)}{1.00 - x} \approx \frac{x^2}{1.00}$$

Thus

$$x^2 \approx 1.8 \times 10^{-5} \quad \text{and} \quad x \approx 4.2 \times 10^{-3}$$

The approximation $1.00 - x \approx 1.00$ is valid by the 5% rule so

$$[H^+] = x = 4.2 \times 10^{-3}\ M$$

The percent dissociation is

$$\frac{[H^+]}{[HC_2H_3O_2]_0} \times 100 = \frac{4.2 \times 10^{-3}}{1.00} \times 100 = 0.42\%$$

b. This is a similar problem except that in this case $[HC_2H_3O_2]_0 = 0.100\ M$. Analysis of the problem leads to the expression

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(x)(x)}{0.100 - x} \approx \frac{x^2}{0.100}$$

Thus

$$x = [H^+] = 1.3 \times 10^{-3}\ M$$

and

$$\text{Percent dissociation} = \frac{1.3 \times 10^{-3}}{0.10} \times 100 = 1.3\%$$

The results in Sample Exercise 14.10 show two important facts. The concentration of H^+ ion at equilibrium is smaller in the 0.10 M acetic acid solution than in the 1.0 M acetic acid solution, as we would expect. However, the percent dissociation is significantly greater in the 0.10 M solution than in the 1.0 M solution. This is a general result. *For solutions of any weak acid HA, $[H^+]$ decreases as $[HA]_0$ decreases, but the percent dissociation increases as $[HA]_0$ decreases.* This phenomenon can be explained as follows.

The more dilute the weak acid solution, the greater the percent dissociation.

Consider the weak acid HA with the initial concentration $[HA]_0$, where at equilibrium

$$[HA] = [HA]_0 - x \approx [HA]_0$$
$$[H^+] = [A^-] = x$$

Thus

$$K_a = \frac{[H^+][A^-]}{[HA]} \approx \frac{(x)(x)}{[HA]_0}$$

Now suppose enough water is added suddenly to dilute the solution by a factor of 10. The new concentrations before any adjustment occurs are

$$[A^-]_{new} = [H^+]_{new} = \frac{x}{10}$$

$$[HA]_{new} = \frac{[HA]_0}{10}$$

and Q, the reaction quotient, is

$$Q = \frac{\left(\frac{x}{10}\right)\left(\frac{x}{10}\right)}{\frac{[HA]_0}{10}} = \frac{1(x)(x)}{10[HA]_0} = \frac{1}{10}K_a$$

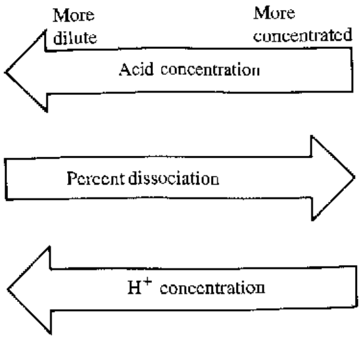


Figure 14.5

The effect of dilution on the percent dissociation and [H$^+$] of a weak acid solution.

Since Q is less than K_a, the system must adjust to the right to reach the new equilibrium position. Thus the percent dissociation increases when the acid is diluted. This behavior is summarized in Fig. 14.5. In Sample Exercise 14.11 we see how the percent dissociation can be used to calculate the K_a value for a weak acid.

Sample Exercise 14.11

Lactic acid ($HC_3H_5O_3$) is a waste product that accumulates in muscle tissue during exertion, leading to pain and a feeling of fatigue. In a 0.100 M aqueous solution, lactic acid is 3.7% dissociated. Calculate the value of K_a for this acid.

Solution

From the small value for the percent dissociation, it is clear that $HC_3H_5O_3$ is a weak acid. Thus the major species in the solution are the undissociated acid and water: $HC_3H_5O_3$ and H_2O. But although $HC_3H_5O_3$ is a weak acid, it is much stronger than water and will be the dominant source of H^+ in the solution. The dissociation reaction is

$$HC_3H_5O_3(aq) \rightleftharpoons H^+(aq) + C_3H_5O_3^-(aq)$$

and the equilibrium expression is

$$K_a = \frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]}$$

The initial and equilibrium concentrations are as follows:

Initial concentration		Equilibrium concentration
$[HC_3H_5O_3]_0 = 0.10\ M$ $[C_3H_5O_3^-]_0 = 0$ $[H^+]_0 \approx 0$	$\xrightarrow{x\ \text{mol/L}}$ $HC_3H_5O_3$ dissociates	$[HC_3H_5O_3] = 0.10 - x$ $[C_3H_5O_3^-] = x$ $[H^+] = x$

The change needed to reach equilibrium can be obtained from the percent dissociation and Equation (14.5). For this acid

$$\text{Percent dissociation} = 3.7\% = \frac{x}{[HC_3H_5O_3]_0} \times 100 = \frac{x}{0.10} \times 100$$

and
$$x = \frac{3.7}{100}(0.10) = 3.7 \times 10^{-3}\ \text{mol/L}$$

Now we can calculate the equilibrium concentrations:

$[HC_3H_5O_3] = 0.10 - x = 0.10\ M$ (to the correct number of significant figures)

$[C_3H_5O_3^-] = [H^+] = x = 3.7 \times 10^{-3}\ M$

These concentrations can now be used to calculate the value of K_a for lactic acid:

$$K_a = \frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]} = \frac{(3.7 \times 10^{-3})(3.7 \times 10^{-3})}{0.10} = 1.4 \times 10^{-4}$$

14.6 | Bases

PURPOSE

- ☐ To introduce equilibria involving strong and weak bases.
- ☐ To show how to calculate pH for basic solutions.

According to the Arrhenius concept, a base is a substance that produces OH^- ions in aqueous solution. According to the Brönsted-Lowry model, a base is a proton acceptor. The bases sodium hydroxide (NaOH) and potassium hydroxide (KOH) fulfill both criteria. They contain OH^- ions in the solid lattice and, behaving as normal electrolytes, dissociate completely when dissolved in aqueous solution:

In a basic solution pH > 7.

$$\mathrm{NaOH}(s) \rightarrow \mathrm{Na}^+(aq) + \mathrm{OH}^-(aq)$$

leaving virtually no undissociated NaOH. Thus a 1.0 *M* NaOH solution really contains 1.0 *M* Na^+ and 1.0 *M* OH^-. Because of their complete dissociation, NaOH and KOH are called **strong bases** in the same sense as we defined strong acids.

All the hydroxides of the Group 1A elements (LiOH, NaOH, KOH, RbOH, and CsOH) are strong bases, but only NaOH and KOH are common laboratory reagents because the lithium, rubidium, and cesium compounds are expensive. The alkaline earth (Group 2A) hydroxides—$Mg(OH)_2$, $Ca(OH)_2$, and $Sr(OH)_2$—are also strong bases. For these compounds, two moles of hydroxide ion are produced for every mole of metal hydroxide dissolved in aqueous solution.

The alkaline earth hydroxides are not very soluble and are used only when the solubility factor is not important. In fact, the low solubility of these bases can sometimes be an advantage. For example, many antacids are suspensions of metal hydroxides such as aluminum hydroxide and magnesium hydroxide. The low solubility of these compounds prevents a large hydroxide ion concentration that would harm the tissues of the mouth, esophagus, and stomach. Yet these suspensions furnish plenty of hydroxide ion to react with the stomach acid, since the salts dissolve as this reaction proceeds.

Calcium hydroxide, $Ca(OH)_2$, often called **slaked lime,** is widely used in industry because it is inexpensive and plentiful. For example, slaked lime is used in scrubbing stack gases to remove sulfur dioxide from the exhaust of power plants and factories. In the scrubbing process a suspension of slaked lime is sprayed into the stack gases to react with sulfur dioxide gas according to the following steps:

Calcium carbonate is also used in scrubbing, as discussed in Section 5.9.

$$\mathrm{SO_2}(g) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2SO_3}(aq)$$
$$\mathrm{Ca(OH)_2}(aq) + \mathrm{H_2SO_3}(aq) \rightleftharpoons \mathrm{CaSO_3}(s) + 2\mathrm{H_2O}(l)$$

Slaked lime is also widely used in water treatment plants for softening hard water, which involves the removal of ions such as Ca^{2+} and Mg^{2+}, which hamper the action of detergents. The softening method most often employed in water treatment plants is the **lime-soda process,** in which *lime* (CaO) and *soda ash* (Na_2CO_3) are added to the water. As we will see in more detail later in this chapter, the CO_3^{2-} ion reacts with water to produce the HCO_3^- ion. When the lime is added to the water, it forms slaked lime

$$\mathrm{CaO}(s) + \mathrm{H_2O}(l) \rightarrow \mathrm{Ca(OH)_2}(aq)$$

which then reacts with the HCO_3^- ion from the added soda ash and a Ca^{2+} ion in the hard water to produce calcium carbonate:

$$Ca(OH)_2(aq) + \underset{\substack{\nearrow \\ \text{From hard water}}}{Ca^{2+}} + 2HCO_3^- \rightarrow 2CaCO_3(s) + 2H_2O(l)$$

Thus for every mole of $Ca(OH)_2$ consumed, 1 mole of Ca^{2+} is removed from the hard water, thereby softening it. Some hard water naturally contains bicarbonate ions. In this case, no soda ash is needed—simply adding the lime produces the softening.

Calculating the pH of a strong base solution is relatively simple, as illustrated in Sample Exercise 14.12.

Sample Exercise 14.12

Calculate the pH of a 5.0×10^{-2} *M* NaOH solution.

Solution

The major species in this solution are

$$Na^+, \quad OH^- \qquad \text{(both from the dissolved NaOH),}$$

and $$H_2O$$

Although autoionization of water also produces OH^- ions, the pH will be dominated by the OH^- ions from the dissolved NaOH. Thus, in the solution

$$[OH^-] = 5.0 \times 10^{-2}\ M$$

and the concentration of H^+ can be calculated from K_w:

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-2}} = 2.0 \times 10^{-13}\ M$$

$$pH = 12.70$$

Note this is a basic solution for which

$$[OH^-] > [H^+] \quad \text{and} \quad pH > 7$$

The added OH^- from the salt has shifted the water autoionization equilibrium

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

to the left, significantly lowering $[H^+]$ compared to that in pure water.

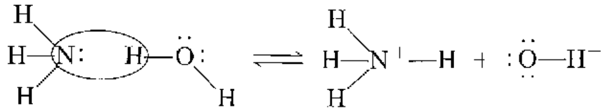
A base does not have to contain hydroxide ion.

Many types of proton acceptors (bases) do not contain the hydroxide ion. However, when dissolved in water, these substances increase the concentration of hydroxide ion because of their reaction with water. For example, ammonia reacts with water as follows:

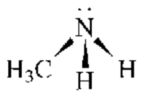
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The ammonia molecule accepts a proton and thus functions as a base. Water is the acid in this reaction. Note that even though the base ammonia contains no hydroxide ion, it still increases the concentration of hydroxide ion to yield a basic solution.

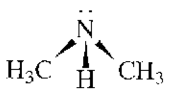
Bases like ammonia typically have at least one unshared pair of electrons that is capable of forming a bond with a proton. The reaction of an ammonia molecule with a water molecule can be represented as follows:



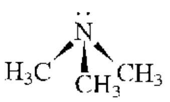
There are many bases like ammonia that produce hydroxide ion by reaction with water. In most of these bases, the lone pair is located on a nitrogen atom. Some examples are



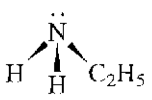
Methylamine



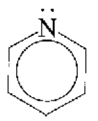
Dimethylamine



Trimethylamine

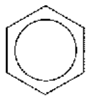


Ethylamine



Pyridine

Note that the first four bases can be thought of as substituted ammonia molecules with hydrogen atoms replaced by methyl (CH_3) or ethyl (C_2H_5) groups. The pyridine molecule is like benzene



except that a nitrogen atom replaces one of the carbon atoms in the ring. The general reaction between a base (B) and water is given by:

$$\underset{\text{Base}}{B(aq)} + \underset{\text{Acid}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{Conjugate}\\\text{acid}}}{BH^+(aq)} + \underset{\substack{\text{Conjugate}\\\text{base}}}{OH^-(aq)} \qquad (14.6)$$

The equilibrium constant for this general reaction is

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

where K_b *always refers to the reaction of a base with water to form the conjugate acid and the hydroxide ion.*

Bases of the type represented by B in Equation (14.6) compete with OH^-, a very strong base, for the H^+ ion. Thus their K_b values tend to be small (for example, for ammonia, $K_b = 1.8 \times 10^{-5}$), and they are called **weak bases.** The values of K_b for some common weak bases are listed in Table 14.3.

Values of K_b for Some Common Weak Bases

Name	Formula	Conjugate acid	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	$CH_3NH_3^+$	4.38×10^{-4}
Ethylamine	$C_2H_5NH_2$	$C_2H_5NH_3^+$	5.6×10^{-4}
Aniline	$C_6H_5NH_2$	$C_6H_5NH_3^+$	3.8×10^{-10}
Pyridine	C_5H_5N	$C_5H_5NH^+$	1.7×10^{-9}

Table 14.3

Refer to the steps for solving weak acid equilibrium problems on page 574. Use the same systematic approach for weak base equilibrium problems.

Typically, pH calculations for solutions of weak bases are very similar to those for weak acids, as illustrated by Sample Exercises 14.13 and 14.14.

Sample Exercise 14.13

Calculate the pH for a 15.0 *M* solution of NH_3 ($K_b = 1.8 \times 10^{-5}$).

Solution

Since ammonia is a weak base, as can be seen from its small K_b value, most of the dissolved NH_3 will remain as NH_3. Thus the major species in solution are

$$NH_3 \quad \text{and} \quad H_2O$$

Both of these substances can produce OH^- according to the reactions:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = 1.8 \times 10^{-5}$$

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad K_w = 1.0 \times 10^{-14}$$

However, the contribution from water can be neglected, since $K_b \gg K_w$. The equilibrium for NH_3 will dominate, and the equilibrium expression to be used is

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

The appropriate concentrations are

Initial concentration (mol/L)		Equilibrium concentration (mol/L)
$[NH_3]_0 = 15.0$ $[NH_4^+]_0 = 0$ $[OH^-]_0 \approx 0$	x mol/L NH_3 reacts with $\xrightarrow{}$ H_2O to reach equilibrium	$[NH_3] = 15.0 - x$ $[NH_4^+] = x$ $[OH^-] = x$

Substituting the equilibrium concentrations in the equilibrium expression and making the usual approximation gives

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(x)(x)}{15.0 - x} \approx \frac{x^2}{15.0}$$

Thus $\qquad x \approx 1.6 \times 10^{-2}$

The 5% rule validates the approximation, and so

$$[OH^-] = 1.6 \times 10^{-2}\ M$$

Since we know that K_w must be satisfied for this solution, we can calculate $[H^+]$ as follows:

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.6 \times 10^{-2}} = 6.3 \times 10^{-13}\ M$$

Therefore

$$pH = 12.20$$

Sample Exercise 14.13 illustrates how a typical weak base equilibrium problem should be solved. Note two additional important points:

1. We calculated $[H^+]$ from K_w and then calculated the pH, but another method is available. The pOH could have been calculated from $[OH^-]$ and then used in Equation (14.3):

$$pK_w = 14.00 = pH + pOH$$
$$pH = 14.00 - pOH$$

2. In a 15.0 M NH_3 solution, the equilibrium concentrations of $NH_4{}^+$ and OH^- are each 1.6×10^{-2} M. Only a small percentage,

$$\frac{1.6 \times 10^{-2}}{15.0} \times 100 = 0.11\%$$

of the ammonia reacts with water. Bottles containing 15.0 M NH_3 solution are often labeled 15.0 M NH_4OH, but as you can see from these results, 15.0 M NH_3 is actually a much more accurate description of the solution contents.

Sample Exercise 14.14

Calculate the pH of a 1.0 M solution of methylamine ($K_b = 4.38 \times 10^{-4}$).

Solution

Since methylamine (CH_3NH_2) is a weak base, the major species in solution are

$$CH_3NH_2 \quad \text{and} \quad H_2O$$

Both are bases; however water can be neglected as a source of OH^-, so the dominant equilibrium is

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3{}^+(aq) + OH^-(aq)$$

and

$$K_b = 4.38 \times 10^{-4} = \frac{[CH_3NH_3{}^+][OH^-]}{[CH_3NH_2]}$$

The concentrations are as follows:

Initial concentration (mol/L)		Equilibrium concentration (mol/L)
$[CH_3NH_2]_0 = 1.0$ $[CH_3NH_3{}^+]_0 = 0$ $[OH^-]_0 \approx 0$	$\xrightarrow[\text{to reach equilibrium}]{x \text{ mol/L } CH_3NH_2 \text{ reacts with } H_2O}$	$[CH_3NH_2] = 1.0 - x$ $[CH_3NH_3{}^+] = x$ $[OH^-] = x$

Substituting the equilibrium concentrations in the equilibrium expression and making the usual approximation gives

$$K_b = 4.38 \times 10^{-4} = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \frac{(x)(x)}{1.0 - x} \approx \frac{x^2}{1.0}$$

$$x \approx 2.1 \times 10^{-2}$$

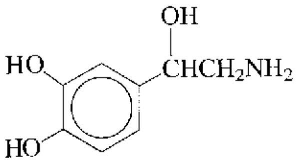
The approximation is valid by the 5% rule, so

$$[OH^-] = x = 2.1 \times 10^{-2}\ M$$
$$pOH = 1.68$$
$$pH = 14.00 - 1.68 = 12.32$$

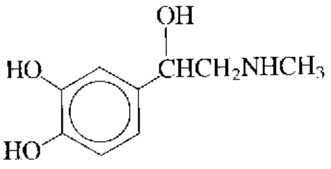
CHEMICAL IMPACT

AMINES

We have seen that many bases have nitrogen atoms with one lone pair and can be viewed as substituted ammonia molecules, with the general formula $R_xNH_{(3-x)}$. Compounds of this type are called **amines.** Amines are widely distributed in animals and plants, and complex amines often serve as messengers or regulators. For example, in the human nervous system, there are two amine stimulants, *norepinephrine* and *adrenaline*.

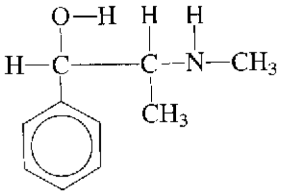


Norepinephrine

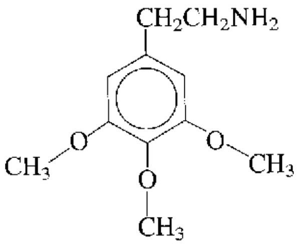


Adrenaline

Ephedrine, widely used as a decongestant, was a known drug in China over 2000 years ago. Indians in Mexico and the Southwest have used the hallucinogen *mescaline*, extracted from peyote cactus, for centuries.



Ephedrine

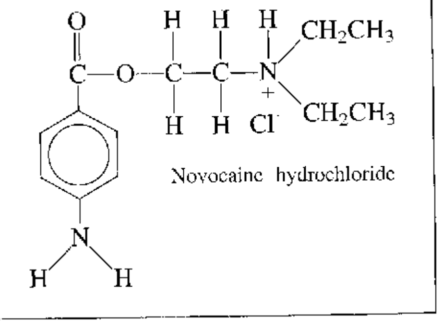


Mescaline

Many other drugs, such as codeine and quinine, are amines, but they are usually not used in their pure amine forms. Instead, they are treated with an acid to become acid salts. An example of an acid salt is ammonium chloride, obtained by the reaction:

$$NH_3 + HCl \rightarrow NH_4Cl$$

Amines can also be protonated in this way. The resulting acid salt, written as AHCl, (where A represents the amine), contains AH^+ and Cl^-. In general, the acid salts are more stable and more soluble in water than the parent amines. For instance, the parent amine of the well-known local anaesthetic *novocaine* is water-insoluble, while the acid salt is much more soluble.



Novocaine hydrochloride

14.7 | Polyprotic Acids

PURPOSE

☐ To describe the dissociation equilibria of acids with more than one acidic proton.

Some important acids, such as sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4), can furnish more than one proton and are called **polyprotic acids.** A polyprotic acid always dissociates in a *stepwise* manner, one proton at a time. For example, the diprotic (two-proton) acid *carbonic acid* (H_2CO_3), which is so important in maintaining a constant pH in human blood, dissociates in the following steps:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.3 \times 10^{-7}$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \qquad K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 5.6 \times 10^{-11}$$

The successive K_a values for the dissociation equilibria are designated K_{a_1} and K_{a_2}. Note that the conjugate base HCO_3^- of the first dissociation equilibrium becomes the acid in the second step.

Carbonic acid is formed when carbon dioxide gas is dissolved in water. In fact, the first dissociation step for carbonic acid is best represented by the reaction

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

since relatively little H_2CO_3 actually exists in solution. However, it is convenient to consider CO_2 in water as H_2CO_3 so that we can treat such solutions using the familiar dissociation reactions for weak acids.

Phosphoric acid is a **triprotic acid** (three protons) that dissociates in the following steps:

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq) \qquad K_{a_1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \qquad K_{a_2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \qquad K_{a_3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.8 \times 10^{-13}$$

For a typical weak polyprotic acid,

$$K_{a_1} > K_{a_2} > K_{a_3}$$

That is, the acid involved at each step of the dissociation is successively weaker, as shown by the stepwise dissociation constants given in Table 14.4. These values indicate that the loss of a second or third proton occurs less readily than the loss of the first proton. This is not surprising; as the negative charge on the acid increases, it becomes more difficult to remove the positively charged proton.

Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid	H_2S	1.0×10^{-7}	1.3×10^{-13}	
Oxalic acid	$H_2C_2O_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$H_2C_6H_6O_6$	7.9×10^{-5}	1.6×10^{-12}	

Table 14.4

Although we might expect the pH calculations for solutions of polyprotic acids to be complicated, the most common cases are surprisingly straightforward. To illustrate, we will consider a typical case, phosphoric acid, and a unique case, sulfuric acid.

Phosphoric Acid

Phosphoric acid is typical of most weak polyprotic acids in that the successive K_a values are very different. For example, the ratios of successive K_a values (from Table 14.4) are

$$\frac{K_{a_1}}{K_{a_2}} = \frac{7.5 \times 10^{-3}}{6.2 \times 10^{-8}} = 1.2 \times 10^5$$

$$\frac{K_{a_2}}{K_{a_3}} = \frac{6.2 \times 10^{-8}}{4.8 \times 10^{-13}} = 1.3 \times 10^5$$

Thus the relative acid strengths are

$$H_3PO_4 \gg H_2PO_4^- \gg HPO_4^{2-}$$

This means that in a solution prepared by dissolving H_3PO_4 in water, *only the first dissociation step makes an important contribution to $[H^+]$*. This greatly simplifies the pH calculations for phosphoric acid solutions, as is illustrated in Sample Exercise 14.15.

For a solution prepared by dissolving a typical polyprotic acid in water, only the first dissociation step is important in determining the pH.

Sample Exercise 14.15

Calculate the pH of a 5.0 *M* H_3PO_4 solution and the equilibrium concentrations of the species H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}.

Solution

The major species in solution are H_3PO_4 and H_2O. None of the dissociation products of H_3PO_4 is written, since the K_a values are all so small that they will be minor species. The dominant equilibrium will be the dissociation of H_3PO_4:

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$$

where $$K_{a_1} = 7.5 \times 10^{-3} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$$

The concentrations are as follows:

Initial concentration (mol/L)		Equilibrium concentration (mol/L)
$[H_3PO_4]_0 = 5.0$ $[H_2PO_4^-]_0 = 0$ $[H^+]_0 \approx 0$	$\xrightarrow[\text{dissociates}]{x \text{ mol/L } H_3PO_4}$	$[H_3PO_4] = 5.0 - x$ $[H_2PO_4^-] = x$ $[H^+] = x$

Substituting the equilibrium concentrations into the expression for K_{a_1} and making the usual approximation gives

$$K_{a_1} = 7.5 \times 10^{-3} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{(x)(x)}{5.0 - x} \approx \frac{x^2}{5.0}$$

Thus

$$x \approx 1.9 \times 10^{-1}$$

Since 1.9×10^{-1} is less than 5% of 5.0, the approximation is acceptable, and

$$[H^+] = x = 0.19\ M$$
$$\text{pH} = 0.72$$

So far, we have determined that

$$[H^+] = [H_2PO_4^-] = 0.19\ M$$

and

$$[H_3PO_4] = 5.0 - x = 4.8\ M$$

The concentration of HPO_4^{2-} can be obtained by using the expression for K_{a_2}:

$$K_{a_2} = 6.2 \times 10^{-8} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

where

$$[H^+] = [H_2PO_4^-] = 0.19\ M$$

Thus

$$[HPO_4^{2-}] = K_{a_2} = 6.2 \times 10^{-8}\ M$$

To calculate $[PO_4^{3-}]$, we use the expression for K_{a_3} and the values of $[H^+]$ and $[HPO_4^{2-}]$ calculated above:

$$K_{a_3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.8 \times 10^{-13} = \frac{0.19[PO_4^{3-}]}{(6.2 \times 10^{-8})}$$

$$[PO_4^{3-}] = \frac{(4.8 \times 10^{-13})(6.2 \times 10^{-8})}{0.19} = 1.6 \times 10^{-19}\ M$$

These results show that the second and third dissociation steps do not make an important contribution to $[H^+]$. This is apparent from the fact that $[HPO_4^{2-}]$ is 6.2×10^{-8} M, which means that only 6.2×10^{-8} mol/L of $H_2PO_4^-$ has dissociated. The value of $[PO_4^{3-}]$ shows that the dissociation of HPO_4^{2-} is even smaller. We must, however, use the second and third dissociation steps to calculate $[HPO_4^{2-}]$ and $[PO_4^{3-}]$ since these steps are the only sources of these ions.

Sulfuric Acid

Sulfuric acid is unique among the common acids in that it is *a strong acid in its first dissociation step and a weak acid in its second step:*

$$H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq) \qquad K_{a_1} \text{ is very large}$$
$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \qquad K_{a_2} = 1.2 \times 10^{-2}$$

Sample Exercise 14.16 illustrates how to calculate the pH for sulfuric acid solutions.

Sample Exercise 14.16

Calculate the pH of a 1.0 M H_2SO_4 solution.

Solution

The major species in the solution are:

$$H^+, \qquad HSO_4^-, \qquad \text{and} \qquad H_2O$$

where the first two ions are produced by the complete first dissociation step of H_2SO_4. The concentration of H^+ in this solution will be at least 1.0 M, since this amount is produced by the first dissociation step of H_2SO_4. We must now answer this question: does the HSO_4^- ion dissociate enough to produce a significant contribution to the concentration of H^+? This question can be answered by calculating the equilibrium concentrations for the dissociation reaction of HSO_4^-:

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

where

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$$

The concentrations are as follows:

Initial concentration (mol/L)		Equilibrium concentration (mol/L)
$[HSO_4^-]_0 = 1.0$	$\xrightarrow[\text{to reach equilibrium}]{x \text{ mol/L } HSO_4^- \text{ dissociates}}$	$[HSO_4^-] = 1.0 - x$
$[SO_4^{2-}]_0 = 0$		$[SO_4^{2-}] = x$
$[H^+]_0 = 1.0$		$[H^+] = 1.0 + x$

Note that $[H^+]_0$ is not equal to zero, as it usually is for a weak acid, because the first dissociation step has already occurred. Substituting the equilibrium concentrations into the expression for K_{a_2} and making the usual approximation gives

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(1.0 + x)(x)}{1.0 - x} \approx \frac{(1.0)(x)}{(1.0)}$$

Thus

$$x \approx 1.2 \times 10^{-2}$$

Since 1.2×10^{-2} is 1.2% of 1.0, the approximation is valid according to the 5%

rule. Note that x is not equal to $[H^+]$ in this case. Instead

$$\begin{aligned}[H^+] &= 1.0\ M + x = 1.0\ M + (1.2 \times 10^{-2})\ M \\ &= 1.0\ M \qquad \text{(to the correct number of significant figures)}\end{aligned}$$

Thus the dissociation of HSO_4^- does not make a significant contribution to the concentration of H^+, and

$$[H^+] = 1.0\ M \quad \text{and} \quad \text{pH} = 0$$

Sample Exercise 14.16 illustrates the most common case for sulfuric acid in which only the first dissociation makes an important contribution to the concentration of H^+. In solutions more dilute than 1.0 M (for example, 0.10 M H_2SO_4), the dissociation of HSO_4^- is important, and solving the problem requires use of the quadratic formula, as shown in Sample Exercise 14.17.

Only in dilute H_2SO_4 solutions does the second dissociation step contribute significantly to $[H^+]$.

Sample Exercise 14.17

Calculate the pH of a 1.00×10^{-2} M H_2SO_4 solution.

Solution

The major species in solution are H^+, HSO_4^-, and H_2O. Proceeding as in Sample Exercise 14.16, we consider the dissociation of HSO_4^-, which leads to the following concentrations:

Initial concentration (mol/L)		Equilibrium concentration (mol/L)
$[HSO_4^-]_0 = 0.0100$ $[SO_4^{2-}]_0 = 0$ $[H^+]_0 = 0.0100$ ↑ from dissociation of H_2SO_4	$\xrightarrow[\text{to reach equilibrium}]{x \text{ mol/L } HSO_4^- \text{ dissociates}}$	$[HSO_4^-] = 0.0100 - x$ $[SO_4^{2-}] = x$ $[H^+] = 0.0100 + x$

Substituting the equilibrium concentrations into the expression for K_{a_2} gives

$$1.2 \times 10^{-2} = K_{a_2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(0.0100 + x)(x)}{(0.0100 - x)}$$

If we make the usual approximation, then $0.010 + x \approx 0.010$ and $0.010 - x \approx 0.010$, and we have

$$1.2 \times 10^{-2} = \frac{(0.0100 + x)(x)}{(0.0100 - x)} \approx \frac{(0.0100)x}{(0.0100)}$$

The calculated value of x is

$$x = 1.2 \times 10^{-2} = 0.012$$

This value is larger than 0.010, clearly a ridiculous result. Thus we cannot make the usual approximation and must instead solve the quadratic equation. The expression

$$1.2 \times 10^{-2} = \frac{(0.0100 + x)(x)}{(0.0100 - x)}$$

leads to

$$(1.2 \times 10^{-2})(0.0100 - x) = (0.0100 + x)(x)$$

$$(1.2 \times 10^{-4}) - (1.2 \times 10^{-2})x = (1.0 \times 10^{-2})x + x^2$$

$$x^2 + (2.2 \times 10^{-2})x - (1.2 \times 10^{-4}) = 0$$

This equation can be solved using the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where $a = 1$, $b = 2.2 \times 10^{-2}$, and $c = -1.2 \times 10^{-4}$. Use of the quadratic formula gives one negative root (which cannot be correct) and one positive root,

$$x = 4.5 \times 10^{-3}$$

Thus

$$[H^+] = 0.0100 + x = 0.0100 + 0.0045 = 0.0145$$

and $$pH = 1.84$$

Note that in this case the second dissociation step produces about half as many H^+ ions as the initial step does.

This problem can also be solved by successive approximations, a method illustrated in Appendix 1.4.

To summarize, a typical weak polyprotic acid has successive K_a values so much smaller than the first value that only the first dissociation step makes a significant contribution to the equilibrium concentration of H^+. This means that the calculation of the pH for a solution of a weak polyprotic acid is identical to that for a solution of a weak monoprotic acid. Sulfuric acid is unique in being a strong acid in its first dissociation step and a weak acid in its second step. For relatively concentrated solutions of sulfuric acid (1.0 *M* or higher), the large concentration of H^+ from the first dissociation step represses the second step, which can be neglected as a contributor of H^+ ions. For dilute solutions of sulfuric acid, the second step does make a significant contribution, and the quadratic equation is used to solve for x.

14.8 Acid-Base Properties of Salts

PURPOSE

- To explain why certain salts give acidic or basic solutions and to show how to calculate the pH of these solutions.

Salt is simply another name for *ionic compound*. When a salt dissolves in water, we assume that it breaks up into its ions, which move about independently, at least in dilute solutions. Under certain conditions these ions can behave as acids or bases. In this section we explore such reactions.

Salts That Produce Neutral Solutions

Recall that the conjugate base of a strong acid has virtually no affinity for protons as compared to that of the water molecule. This is why strong acids completely dissociate in aqueous solution. Thus, when anions such as Cl^- and NO_3^- are placed in water, they do not combine with H^+ and have no effect on the pH. Cations such as K^+ and Na^+ from strong bases have no affinity for H^+ nor can they produce H^+, and so they too have no effect on the pH of an aqueous solution. *Salts that consist of the cations of strong bases and the anions of strong acids have no effect on $[H^+]$ when dissolved in water*. This means that aqueous solutions of salts such as KCl, NaCl, $NaNO_3$, and KNO_3 are neutral (have a pH of 7).

The salt of a strong acid and a strong base gives a neutral solution.

Salts That Produce Basic Solutions

In an aqueous solution of sodium acetate ($NaC_2H_3O_2$), the major species are:

$$Na^+, \quad C_2H_3O_2^-, \quad \text{and} \quad H_2O$$

What are the acid-base properties of each component? The Na^+ ion has neither acid nor base properties. The $C_2H_3O_2^-$ ion is the conjugate base of acetic acid, a weak acid. This means that $C_2H_3O_2^-$ has a significant affinity for a proton and is a base. Finally, water is a weakly amphoteric substance.

The pH of this solution will be determined by the $C_2H_3O_2^-$ ion. Since $C_2H_3O_2^-$ is a base, it will react with the best proton donor available. In this case, water is the *only* source of protons, and the reaction between the acetate ion and water is

$$C_2H_3O_2^-(aq) + H_2O(l) \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq) \qquad (14.7)$$

Note that this reaction, which yields a basic solution, involves a *base reacting with water to produce hydroxide ion and a conjugate acid*. We have defined K_b as the equilibrium constant for such a reaction. In this case

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]}$$

The value of K_a for acetic acid is well known (1.8×10^{-5}). But how can we obtain the K_b value for the acetate ion? The answer lies in the relationships among K_a, K_b, and K_w. Note that when the expression for K_a for acetic acid is multiplied by the expression for K_b for the acetate ion, the result is K_w:

$$K_a \times K_b = \frac{[H^+]\cancel{[C_2H_3O_2^-]}}{\cancel{[HC_2H_3O_2]}} \times \frac{\cancel{[HC_2H_3O_2]}[OH^-]}{\cancel{[C_2H_3O_2^-]}} = [H^+][OH^-] = K_w$$

This is a very important result. For any weak acid and its conjugate base,

$$K_a \times K_b = K_w$$

Thus, when either K_a or K_b is known, the other can be calculated. For the acetate ion,

$$K_b = \frac{K_w}{K_a \text{ (for } HC_2H_3O_2)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

This is the K_b value for the reaction described by equation (14.7). Note that it is obtained from the K_a value of the parent weak acid, in this case acetic acid. The

A basic solution is formed if the anion of the salt is the conjugate base of a weak acid.

sodium acetate solution is an example of an important general case. *For any salt whose cation has neutral properties (such as Na^+ or K^+) and whose anion is the conjugate base of a weak acid, the aqueous solution will be basic.* The K_b value for the anion can be obtained from the relationship $K_b = K_w/K_a$. Equilibrium calculations of this type are illustrated in Sample Exercise 14.18.

Sample Exercise 14.18

Calculate the pH of a 0.30 M NaF solution. The K_a value for HF is 7.2×10^{-4}.

Solution

The major species in solution are: Na^+, F^-, and H_2O.

Since HF is a weak acid, the F^- ion must have a significant affinity for protons, and the dominant reaction will be

$$F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$$

which yields the K_b expression

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

The value of K_b can be calculated from K_w and the K_a value for HF:

$$K_b = \frac{K_w}{K_a \text{ (for HF)}} = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$$

The concentrations are as follows:

Initial concentration (mol/L)		Equilibrium concentration (mol/L)
$[F^-]_0 = 0.30$ $[HF]_0 = 0$ $[OH^-]_0 \approx 0$	$\xrightarrow[\text{H}_2\text{O to reach equilibrium}]{x \text{ mol/L } F^- \text{ reacts with}}$	$[F^-] = 0.30 - x$ $[HF] = x$ $[OH^-] = x$

Thus $\qquad K_b = 1.4 \times 10^{-11} = \dfrac{[HF][OH^-]}{[F^-]} = \dfrac{(x)(x)}{0.30 - x} \approx \dfrac{x^2}{0.30}$

$$x \approx 2.0 \times 10^{-6}$$

The approximation is valid by the 5% rule, and so

$$[OH^-] = x = 2.0 \times 10^{-6}\ M$$
$$pOH = 5.69$$
$$pH = 14.00 - 5.69 = 8.31$$

As expected, the solution is basic.

Base Strength in Aqueous Solution

To emphasize the concept of base strength, let us consider the basic properties of the cyanide ion. One relevant reaction is the dissociation of hydrocyanic acid in water:

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq) \qquad K_a = 6.2 \times 10^{-10}$$

Since HCN is such a weak acid, CN^- appears to be a *strong* base, showing a very high affinity for H^+ *compared to H_2O*, with which it is competing. However, we also need to look at the reaction in which cyanide ion reacts with water:

$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$$

where

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$$

In this reaction CN^- appears to be a weak base; the K_b value is only 1.6×10^{-5}. What accounts for this apparent difference in base strength? The key idea is that in the reaction of CN^- with H_2O, *CN^- is competing with OH^- for H^+, instead of competing with H_2O*, as it does in the HCN dissociation reaction. These equilibria show the following relative base strengths:

$$OH^- > CN^- > H_2O$$

Similar arguments can be made for other "weak" bases, such as ammonia, the acetate ion, the fluoride ion, and so on.

Salts That Produce Acidic Solutions

Some salts produce acidic solutions when dissolved in water. For example, when solid NH_4Cl is dissolved in water, NH_4^+ and Cl^- ions are present, with NH_4^+ behaving as a weak acid:

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

The Cl^- ion, having virtually no affinity for H^+ in water, does not affect the pH of the solution.

In general, *salts of which the cation is the conjugate acid of a weak base produce acidic solutions.*

Sample Exercise 14.19

Calculate the pH of a 0.10 *M* NH_4Cl solution. The K_b value for NH_3 is 1.8×10^{-5}.

Solution

The major species in solution are: NH_4^+, Cl^-, and H_2O. Note that both NH_4^+ and H_2O can produce H^+. The dissociation reaction for the NH_4^- ion is

$$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$$

for which

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

Note that although the K_b value for NH_3 is given, the reaction corresponding to K_b is not appropriate here, since NH_3 is not a major species in the solution. Instead, the given value of K_b is used to calculate K_a for NH_4^+ from the relationship:

$$K_a \times K_b = K_w$$

Thus

$$K_a \text{ (for } NH_4^+) = \frac{K_w}{K_b \text{ (for } NH_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Although NH_4^+ is a very weak acid, as indicated by its K_a value, it is stronger than H_2O and thus will dominate in the production of H^+. Thus we will focus on the dissociation reaction of NH_4^+ to calculate the pH in this solution.

We solve the weak acid problem in the usual way:

Initial concentration (mol/L)		Equilibrium concentration (mol/L)
$[NH_4^+]_0 = 0.10$ $[NH_3]_0 = 0$ $[H^+]_0 \approx 0$	$\xrightarrow[\text{to reach equilibrium}]{x \text{ mol/L } NH_4^+ \text{ dissociates}}$	$[NH_4] = 0.10 - x$ $[NH_3] = x$ $[H^+] \approx x$

Thus

$$5.6 \times 10^{-10} = K_a = \frac{[H^+][NH_3]}{[NH_4^+]} = \frac{(x)(x)}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x \approx 7.5 \times 10^{-6}$$

The approximation is valid by the 5% rule, so

$$[H^+] = x = 7.5 \times 10^{-6}\ M \quad \text{and} \quad pH = 5.13$$

A second type of salt that produces an acidic solution is one that contains a *highly charged metal ion*. For example, when solid aluminum chloride ($AlCl_3$) is dissolved in water, the resulting solution is significantly acidic. Although the Al^{3+} ion is not itself a Brönsted-Lowry acid, the hydrated ion $Al(H_2O)_6^{3+}$ formed in water is a weak acid:

$$Al(H_2O)_6^{3+}(aq) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + H^+(aq)$$

The high charge on the metal ion polarizes the O—H bonds in the attached water molecules, making the hydrogens in these water molecules more acidic than those in free water molecules. Typically, the higher the charge on the metal ion, the stronger the acidity of the hydrated ion.

Section 14.9 contains a further discussion of the acidity of hydrated ions.

Sample Exercise 14.20

Calculate the pH of a 0.010 *M* $AlCl_3$ solution. The K_a value for $Al(H_2O)_6^{3+}$ is 1.4×10^{-5}).

Solution

The major species in solution are: $Al(H_2O)_6^{3+}$, Cl^-, and H_2O. Since the $Al(H_2O)_6^{3+}$ ion is a stronger acid than water, the dominant equilibrium is

$$Al(H_2O)_6^{3+} \rightleftharpoons Al(OH)(H_2O)_5^{2+} + H^+$$

and

$$1.4 \times 10^{-5} = K_a = \frac{[Al(OH)(H_2O)_5^{2+}][H^+]}{[Al(H_2O)_6^{3+}]}$$

This is a typical weak acid problem which we can solve with the usual procedures.

Initial concentration (mol/L)		Equilibrium concentration (mol/L)
$[Al(H_2O)_6^{3+}]_0 = 0.010$ $[Al(OH)(H_2O)_5^{2+}]_0 = 0$ $[H^+]_0 \approx 0$	$\xrightarrow{x \text{ mol/L}}$ $Al(OH_2)_6^{3+}$ dissociates to reach equilibrium	$[Al(H_2O)_6^{3+}] = 0.010 - x$ $[Al(OH)(H_2O)_5^{2+}] = x$ $[H^+] = x$

Thus

$$1.4 \times 10^{-5} = K_a = \frac{[Al(OH)(H_2O)_5^{2+}][H^+]}{[Al(H_2O)_6^{3+}]} = \frac{(x)(x)}{0.010 - x} \approx \frac{x^2}{0.010}$$

$$x \approx 3.7 \times 10^{-4}$$

Since the approximation is valid by the 5% rule,

$$[H^+] = x = 3.7 \times 10^{-4}\ M \quad \text{and} \quad pH = 3.43$$

So far we have considered salts in which only one of the ions has acidic or basic properties. For many salts, such as ammonium acetate ($NH_4C_2H_3O_2$), both ions can affect the pH of the aqueous solution. Because the equilibrium calculations for these cases can be quite complicated, we will consider only the qualitative aspects of such problems. We can predict whether the solution will be basic, acidic, or neutral by comparing the K_a value for the acidic ion to the K_b value for the basic ion. If the K_a value for the acidic ion is larger than the K_b value for the basic ion, the solution will be acidic. If the K_b value is larger than the K_a value, the solution will be basic. Equal K_a and K_b values mean a neutral solution. These facts are summarized in Table 14.5.

Qualitative Prediction of pH for Solutions of Salts for Which Both Cation and Anion Have Acidic or Basic Properties	
Relative K_a and K_b values for the ions in solution	pH
$K_a > K_b$	$pH < 7$ (acidic)
$K_b > K_a$	$pH > 7$ (basic)
$K_a = K_b$	$pH = 7$ (neutral)

Table 14.5

Sample Exercise 14.21

Predict whether an aqueous solution of each of the following salts will be acidic, basic, or neutral:

a. $NH_4C_2H_3O_2$ **b.** NH_4CN **c.** $Al_2(SO_4)_3$

Solution

a. The ions in solution are NH_4^+ and $C_2H_3O_2^-$. As we mentioned previously, K_a for NH_4^+ is 5.6×10^{-10}, and K_b for $C_2H_3O_2^-$ is 5.6×10^{-10}. Thus K_a for NH_4^+ is equal to K_b for $C_2H_3O_2^-$, and the solution will be neutral (pH = 7).

b. The solution will contain NH_4^+ and CN^- ions. The K_a value for NH_4^+ is 5.6×10^{-10} and

$$K_b \text{ (for } CN^-) = \frac{K_w}{K_a \text{ (for HCN)}} = 1.6 \times 10^{-5}$$

Since K_b for CN^- is much larger than K_a for NH_4^+, CN^- is a much stronger base than NH_4^+ is an acid. This solution will be basic.

c. The solution will contain $Al(H_2O)_6^{3+}$ and SO_4^{2-} ions. The K_a value for $Al(H_2O)_6^{3+}$ is 1.4×10^{-5}, as given in Sample Exercise 14.20. We must calculate K_b for SO_4^{2-}. The HSO_4^- ion is the conjugate acid of SO_4^{2-}, and its K_a value is K_{a_2} for sulfuric acid, or 1.2×10^{-2}. Therefore

$$K_b \text{ (for } SO_4^{2-}) = \frac{K_w}{K_{a_2} \text{ (for sulfuric acid)}} = \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-2}} = 8.3 \times 10^{-13}$$

This solution will be acidic, since K_a for $Al(H_2O)_6^{3+}$ is much greater than K_b for SO_4^{2-}.

The acid-base properties of aqueous solutions of various salts are summarized in Table 14.6.

Acid-Base Properties of Various Types of Salts

Type of salt	Examples	Comment	pH of solution
Cation is from strong base; anion is from strong acid	KCl, KNO_3, NaCl, $NaNO_3$	Neither ion acts as an acid or a base	Neutral
Cation is from strong base; anion is from weak acid	$NaC_2H_3O_2$, KCN, NaF	Anion acts as a base; cation has no effect on pH	Basic
Cation is conjugate acid of weak base, anion is from strong acid	NH_4Cl, NH_4NO_3	Cation acts as acid; anion has no effect on pH	Acidic
Cation is conjugate acid of weak base; anion is conjugate base of weak acid	$NH_4C_2H_3O_2$, NH_4CN	Cation acts as an acid; anion acts as a base	Acidic if $K_a > K_b$, basic if $K_b > K_a$, neutral if $K_a = K_b$
Cation is highly charged metal ion; anion is from strong acid	$Al(NO_3)_3$, $FeCl_3$	Hydrated cation acts as an acid; anion has no effect on pH	Acidic

Table 14.6

14.9 The Effect of Structure on Acid-Base Properties

PURPOSE

☐ To show how bond strength and polarity affect acid-base properties.

We have seen that when a substance is dissolved in water, it produces an acidic solution if it can donate protons and produces a basic solution if it can accept protons. What structural properties of a molecule cause it to behave as an acid or as a base?

Any molecule containing a hydrogen atom is potentially an acid. However, many such molecules show no acidic properties. For example, molecules containing C—H bonds, such as chloroform ($CHCl_3$) and nitromethane (CH_3NO_2), do not produce acidic aqueous solutions because a C—H bond is both strong and nonpolar and thus there is no tendency to donate protons. On the other hand, although the H—Cl bond in gaseous hydrogen chloride is slightly stronger than a C—H bond, it is much more polar, and this molecule readily dissociates when dissolved in water.

Thus there are two main factors that determine whether a molecule containing an X—H bond will behave as a Brönsted-Lowry acid: the strength of the bond and the polarity of the bond.

The importance of these factors is clearly demonstrated by the relative acid strengths of the hydrogen halides. The bond polarities vary as shown

$$\underset{\text{Most polar}}{\underset{\uparrow}{\mathrm{H{-}F}}} > \mathrm{H{-}Cl} > \mathrm{H{-}Br} > \underset{\text{Least polar}}{\underset{\uparrow}{\mathrm{H{-}I}}}$$

because electronegativity decreases going down the group. Based on the high polarity of the H—F bond, we might expect hydrogen fluoride to be a very strong acid. In fact, among HX molecules, HF is the only weak acid ($K_a = 7.2 \times 10^{-4}$) when dissolved in water. The H—F bond is unusually strong, as shown in Table 14.7. Because it is so difficult to break, the HF molecules in water dissociate only to a small extent.

Bond Strengths and Acid Strengths for Hydrogen Halides

H—X bond	Bond strength (kJ/mol)	Acid strength in water
H—F	565	Weak
H—Cl	427	Strong
H—Br	363	Strong
H—I	295	Strong

Table 14.7

Another important class of acids are the oxyacids, which as we saw in Section 14.2 characteristically contain the grouping H—O—X. Several series of oxyacids are listed in Table 14.8 with their K_a values. Note from these data that for a given series the acid strength increases with an increase in the number of oxygen atoms attached to the central atom. For example, in the series containing chlorine and a varying number of oxygen atoms, HOCl is a weak acid, but the acid strength is successively greater as the number of oxygen atoms increases. This happens because the very electronegative oxygen atoms are able to draw electrons away from the chlorine atom and the O—H bond, as shown in Fig. 14.6. The net effect is to both polarize and weaken the O—H bond; this effect is more important as the number of attached oxygen atoms increases. This means that a proton is most readily produced by the molecule with the largest number of attached oxygen atoms ($HClO_4$).

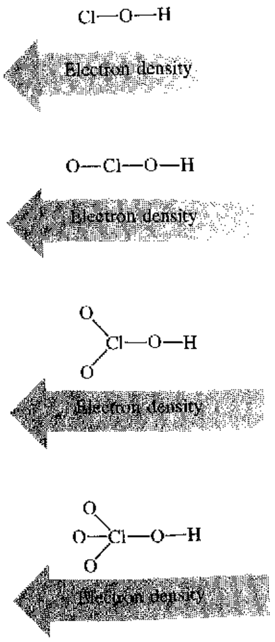


Figure 14.6

The effect of the number of attached oxygens on the H—O bond in a series of chlorine oxyacids. As the number of oxygen atoms attached to the chlorine atom increases, they become more effective at withdrawing electron density from the H—O bond, thereby weakening and polarizing it. This increases the tendency for the molecule to produce a proton, and so its acid strength increases.

Several Series of Oxyacids and Thier K_a Values

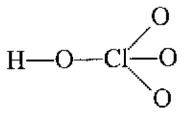
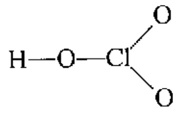
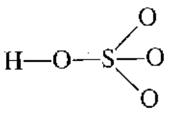
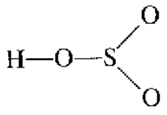
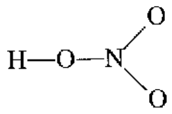
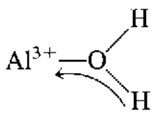
Oxyacid	Structure	K_a value
$HClO_4$		Large (~10^7)
$HClO_3$		~1
$HClO_2$	H—O—Cl—O	1.2×10^{-2}
$HClO$	H—O—Cl	3.5×10^{-8}
H_2SO_4		Large
H_2SO_3		1.5×10^{-2}
HNO_3		Large
HNO_2	H—O—N—O	4.0×10^{-4}

Table 14.8

This type of behavior is also observed for hydrated metal ions. Earlier in this chapter we saw that highly charged metal ions such as Al^{3+} produce acidic solutions. The acidity of the water molecules attached to the metal ion is increased by the attraction of electrons to the positive metal ion:



The greater the charge on the metal ion, the more acidic the hydrated ion becomes.

For acids containing the H—O—X grouping, the greater the ability of X to draw electrons toward itself, the greater is the acidity of the molecule. Since the electronegativity of X reflects its ability to attract the electrons involved in bonding, we might expect acid strength to depend on the electronegativity of X. In fact, there is an excellent correlation between the electronegativity of X and the acid strength for oxyacids, as shown in Table 14.9.

Comparison of Electronegativity of X and K_a value for a Series of Oxyacids

Acid	X	Electronegativity of X	K_a for acid
HOCl	Cl	3.0	4×10^{-8}
HOBr	Br	2.8	2×10^{-9}
HOI	I	2.5	2×10^{-11}
$HOCH_3$	CH_3	2.3 (for carbon in CH_3)	~0

Table 14.9

14.10 Acid-Base Properties of Oxides

PURPOSE

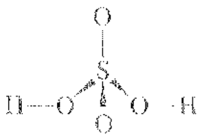
☐ To show how to predict whether an oxide will produce an acidic or basic solution.

We have just seen that molecules containing the grouping H—O—X can behave as acids and that the acid strength depends on the electron-withdrawing ability of X. But substances with this grouping can also behave as bases, if hydroxide ion instead of a proton is produced. What determines which behavior will occur? The answer lies mainly in the nature of the O—X bond. If X has a relatively high electronegativity, the O—X bond will be covalent and strong. When the compound containing the H—O—X grouping is dissolved in water, the O—X bond will remain intact. It will be the polar and relatively weak H—O bond that will tend to break, releasing a proton. On the other hand, if X has a very low electronegativity, the O—X bond will be ionic and subject to being broken in polar water. Examples are the ionic substances NaOH and KOH that dissolve in water to give the metal cation and the hydroxide ion.

A compound containing the H—O—X group will produce an acidic solution in water if the O—X bond is strong and covalent. If the O—X bond is ionic, the compound will produce a basic solution in water.

We can use these principles to explain the acid-base behavior of oxides when they are dissolved in water. For example, when a covalent oxide such as sulfur trioxide is dissolved in water, an acidic solution results because sulfuric acid is formed:

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$



The structure of H_2SO_4 is shown in the margin. In this case, the strong, covalent O—S bonds remain intact and the H—O bonds break to produce protons. Other common covalent oxides that react with water to form acidic solutions are sulfur dioxide, carbon dioxide, and nitrogen dioxide, as shown by the following reactions:

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$

$$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$$

Thus, when a covalent oxide dissolves in water, an acidic solution forms. These oxides are called **acidic oxides.**

On the other hand, when an ionic oxide dissolves in water, a basic solution results, as shown by the following reactions:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$$

$$K_2O(s) + H_2O(l) \rightarrow 2KOH(aq)$$

These reactions can be explained by recognizing that the oxide ion has a high affinity for protons and reacts with water to produce hydroxide ions:

$$O^{2-}(aq) + H_2O(l) \rightarrow 2OH^-(aq)$$

Thus the most ionic oxides, such as those of the Group 1A and 2A metals, produce basic solutions when they are dissolved in water. As a result, these oxides are called **basic oxides.**

14.11 The Lewis Acid-Base Model

PURPOSE

☐ To define acids and bases in terms of electron pairs.

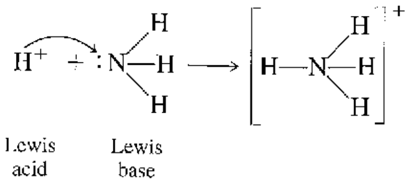
We have seen that the first successful conceptualization of acid-base behavior was proposed by Arrhenius. This useful but limited model was replaced by the more general Brönsted-Lowry model. An even more general model for acid-base behavior was suggested by G. N. Lewis in the early 1920s. A **Lewis acid** is an *electron-pair acceptor,* and a **Lewis base** is an *electron-pair donor.* The three models are summarized in Table 14.10.

Three Models for Acids and Bases

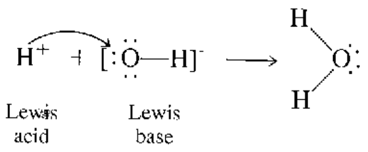
Model	Definition of acid	Definition of base
Arrhenius	H^- producer	OH^- producer
Brönsted-Lowry	H^+ donor	H^+ acceptor
Lewis	Electron-pair acceptor	Electron-pair donor

Table 14.10

Note that Brönsted-Lowry acid-base reactions (proton donor–proton acceptor reactions) are encompassed by the Lewis model. For example, the reaction between a proton and an ammonia molecule

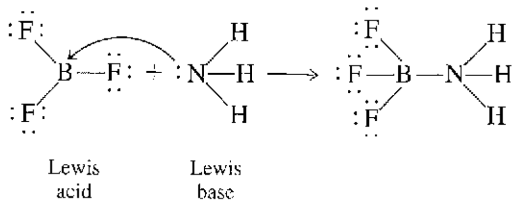


can be represented as a reaction between an electron-pair acceptor (H^+) and an electron-pair donor (NH_3). The same holds true for a reaction between a proton and a hydroxide ion:



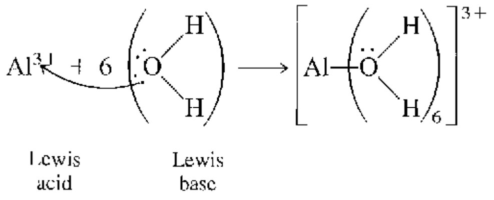
The real value of the Lewis model for acids and bases is that it covers many reactions that do not involve Brönsted-Lowry acids. For example, consider the gas-phase reaction between boron trifluoride and ammonia:

The Lewis model encompasses the Brönsted-Lowry model, but the reverse is not true.



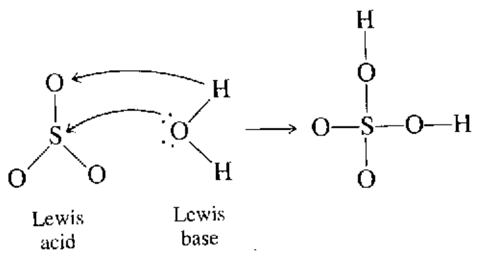
Here the electron-deficient BF_3 molecule (there are only six electrons around the boron) completes its octet by reacting with NH_3, which has a lone pair of electrons. In fact, as mentioned in Chapter 8, the electron deficiency of boron trifluoride makes it very reactive toward any electron-pair donor. That is, it is a strong Lewis acid.

The hydration of a metal ion, such as Al^{3+}, can be also viewed as a Lewis acid-base reaction:



Here the Al^{3+} ion accepts one electron pair from each of six water molecules.

In addition, the reaction between a covalent oxide and water to form a Brönsted-Lowry acid can be defined as a Lewis acid-base reaction. An example is the reaction between sulfur trioxide and water:



Note that as the water molecule attaches to sulfur trioxide, a proton shift occurs to form sulfuric acid.

Sample Exercise 14.22

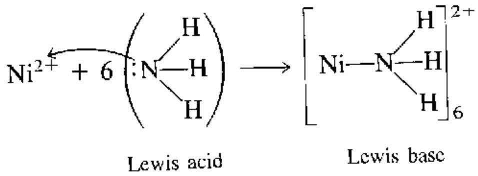
For each reaction, identify the Lewis acid and base.

a. $Ni^{2+}(aq) + 6NH_3(aq) \rightarrow Ni(NH_3)_6^{2+}(aq)$

b. $H^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq)$

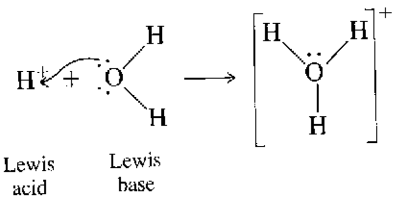
Solution

a. Each NH_3 molecule donates an electron pair to the Ni^{2+} ion:



The nickel(II) ion is the Lewis acid, and ammonia is the Lewis base.

b. The proton is the Lewis acid and the water molecule is the Lewis base:



14.12 Strategy for Solving Acid-Base Problems—A Summary

In this chapter we have encountered many different situations involving aqueous solutions of acids and bases, and in the next chapter we will encounter still more. In solving for the equilibrium concentrations in these aqueous solutions, it is tempting to create a pigeonhole for each possible situation and to memorize the procedures necessary to deal with that particular case. This approach is just not practical, and usually leads to frustration: too many pigeonholes are required and there seems to be an infinite number of cases. But you can handle any case successfully by taking a systematic, patient, and thoughtful approach. When analyzing an acid-base equilibrium problem, do *not* ask yourself how a memorized solution can be used to solve the problem. Instead, ask this question: *what are the major species in the solution and what is their chemical behavior?*

The most important part of doing a complicated acid-base equilibrium problem is the analysis you do at the beginning of a problem:

What major species are present?

Does a reaction occur that can be assumed to go to completion?

What equilibrium dominates the solution?

Let the problem guide you. Be patient.

The following steps outline a general strategy for solving problems involving acid-base equilibria.

Solving Acid-Base Problems

STEP 1
List the major species in solution.

STEP 2
Look for reactions that can be assumed to go to completion, for example, a strong acid dissociating or H^+ reacting with OH^-.

STEP 3
For a reaction that can be assumed to go to completion:

a. Determine the concentrations of the products.
b. Write down the major species in solution after the reaction.

STEP 4
Look at each major component of the solution and decide if it is an acid or a base.

STEP 5
Pick the equilibrium that will control the pH. Use known values of the dissociation constants for the various species to help decide on the dominant equilibrium.

a. Write the equation for the reaction and the equilibrium expression.
b. Compute the initial concentrations (assuming the dominant equilibrium has not yet occurred, that is, no acid dissociation, etc.).
c. Define x.
d. Compute the equilibrium concentrations in terms of x.
e. Substitute the concentrations in the equilibrium expression and solve for x.
f. Check the validity of the approximation.
g. Calculate the pH and other concentrations as required.

Although these steps may seem somewhat cumbersome, especially for simpler problems, they will become increasingly helpful as the aqueous solutions become more complicated. If you develop the habit of approaching acid-base problems systematically, the more complex cases will be much easier to manage.

Summary

In this chapter we have developed several models of acid-base behavior and have applied fundamental equilibrium principles to calculate the pH values for solutions of acids and bases.

Arrhenius postulated that acids produce H^+ ions in solutions and bases produce OH^- ions. The Brönsted-Lowry model is more general: an acid is a proton donor, and a base is a proton acceptor. Water acts as a Brönsted-Lowry base when it accepts a proton from an acid to form a hydronium ion:

$$\underset{\text{Acid}}{HA(aq)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{Conjugate}\\\text{acid}}}{H_3O^+(aq)} + \underset{\substack{\text{Conjugate}\\\text{base}}}{A^-(aq)}$$

A conjugate base is everything that remains of the acid molecule after the proton is lost. A conjugate acid is formed when a proton is transferred to the base. Two substances related in this way are called a conjugate acid-base pair.

The equilibrium expression for the dissociation of an acid in water is

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

where H_3O^+ is simplified to H^+, $[H_2O]$ is not included because it is assumed to be constant, and K_a is called the acid dissociation constant. The strength of an acid is defined by the position of the dissociation equilibrium. A small value of K_a denotes a weak acid, one that does not dissociate to any great extent in aqueous solution. A strong acid is one for which the dissociation equilibrium lies far to the right—the K_a value is very large.

Strong acids such as nitric, hydrochloric, sulfuric, and perchloric acids have weak conjugate bases, which have a low affinity for a proton. The strength of an acid is inversely related to the strength of its conjugate base.

Water is an amphoteric substance because it can behave either as an acid or as a base. The autoionization of water reveals this property, since one water molecule transfers a proton to another water molecule to produce a hydronium ion and a hydroxide ion:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

This leads to the equilibrium expression

$$K_w = [H^+][OH^-]$$

where K_w is called the ion-product constant. It has been experimentally shown that at 25°C in pure water $[H^+] = [OH^-] = 1.0 \times 10^{-7}\ M$. Thus at 25°C

$$K_w = 1.0 \times 10^{-14}$$

In an acidic solution, $[H^+]$ is greater than $[OH^-]$. In a basic solution, $[OH^-]$ is greater than $[H^+]$. In a neutral solution, $[H^+]$ is equal to $[OH^-]$.

To describe $[H^+]$ in aqueous solutions, we often use the pH scale, where

$$pH = -\log[H^+]$$

Since pH is a log scale based on 10, the pH changes by 1 for every change by a power of 10 in $[H^+]$. Because pH is defined as $-\log[H^+]$, the pH decreases as $[H^+]$ increases.

The percent dissociation of a weak acid is defined as follows:

$$\text{Percent dissociation} = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \times 100$$

This is another measure of the strength of an acid: the larger the percent dissociation, the stronger the acid. As $[HA]_0$ decreases, $[H^+]$ decreases, but the percent dissociation increases. That is, dilution causes an increase in the percent dissociation.

Strong bases are hydroxide salts, such as NaOH or KOH, that dissociate completely in water. Bases do not have to contain the hydroxide ion; they can be species that remove a proton from water, producing the hydroxide ion. For example, ammonia is a base because it can accept a proton from water

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The equilibrium expression is

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

where K_b always refers to a reaction in which a base reacts with water to produce the conjugate acid and hydroxide ion. Because bases like ammonia must compete with the hydroxide ion for the proton, values of K_b for these bases are typically much less than 1, and these substances are called weak bases.

A polyprotic acid is an acid with more than one acidic proton, which dissociate in a stepwise fashion with a K_a value for each step. Typically, for a weak polyprotic acid

$$K_{a_1} > K_{a_2} > K_{a_3}$$

Sulfuric acid is unique in that it is a strong acid in the first dissociation step and a weak acid in the second step.

Salts can exhibit neutral, acidic, or basic properties when dissolved in water. Salts that contain the cations of strong bases and the anions of strong acids produce neutral aqueous solutions. A basic solution is produced when the dissolved salt has a neutral cation and an anion that is the conjugate base of a weak acid. An acidic solution is produced when the dissolved salt has a cation that is the conjugate acid of a weak base and a neutral anion. Acidic solutions are also produced by salts containing a highly charged metal cation. For example, the hydrated ion $Al(H_2O)_6^{3+}$ is a weak acid.

Most substances that function as acids or bases contain the H—O—X grouping. Molecules where the O—X bond is strong tend to behave as acids, especially when X is highly electronegative, because the X—O bond is polarized and weakened. When X has low electronegativity (if X is a metal, for example), the O—X bond tends to be ionic and hydroxide ion forms when these substances are dissolved in water.

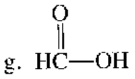
The Lewis model for acids and bases generalizes the concept of acid-base behavior in terms of electron pairs. A Lewis acid is an electron-pair acceptor, and a Lewis base is an electron-pair donor. The value of the Lewis model is that it covers many reactions that do not involve Brönsted-Lowry acids and bases.

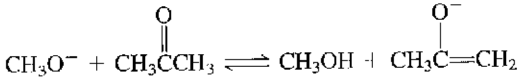
Key Terms

Arrhenius concept (14.1)
Brönsted-Lowry model
hydronium ion
conjugate base
conjugate acid
conjugate acid-base pair
acid dissociation constant
strong acid (14.2)
weak acid
diprotic acid
oxyacids
organic acids
carboxyl group
monoprotic acid
amphoteric substance
autoionization
ion-product constant
pH scale (14.3)
major species (14.4)
percent dissociation (14.5)
strong bases (14.6)
slaked lime
lime-soda process
weak base
amine
polyprotic acid (14.7)
triprotic acid
salt (14.8)
acidic oxide (14.10)
basic oxide
Lewis acid (14.11)
Lewis base

Exercises

Nature of Acids and Bases

1. Classify each of the following as a strong acid, weak acid, strong base, or a weak base:
a. HNO_2
b. H_3PO_4
c. CH_3NH_2
d. NaOH
e. NH_3
f. HF
g. 
$HC(=O){-}OH$
h. $H_2NCH_2CH_2NH_2$
i. H_2SO_4

2. For each of the following reactions, identify the acid, the base, the conjugate base, and the conjugate acid:
a. $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$
b. 
$CH_3O^- + CH_3C(=O)CH_3 \rightleftharpoons CH_3OH + CH_3C(O^-){=}CH_2$
c. $H_2S + NH_3 \rightleftharpoons HS^- + NH_4^+$
d. $H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$
e. $H^+ + OH^- \rightleftharpoons H_2O$
f. $H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$
g. $H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$
h. $H_2PO_4^- + H_2PO_4^- \rightleftharpoons H_3PO_4 + HPO_4^{2-}$
i. $Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^+$
j. $HCN + CO_3^{2-} \rightleftharpoons CN^- + HCO_3^-$
k. $CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+$

3. Write the dissociation reaction and the corresponding equilibrium expression for each of the following acids in water:
a. H_3PO_4
b. $H_2PO_4^-$
c. HPO_4^{2-}
d. HNO_2
e. $Ti(H_2O)_6^{4+}$
f. HCN
g. acetic acid, CH_3CO_2H ($HC_2H_3O_2$)
h. phenol, C_6H_5OH
i. benzoic acid, $C_6H_5CO_2H$
j. glycine, $H_2NCH_2CO_2H$

4. Write the reaction and the corresponding K_b equilibrium expression for each of the following substances acting as bases in water:
a. PO_4^{3-}
b. HPO_4^{2-}
c. $H_2PO_4^-$
d. NH_3
e. CN^-
f. pyridine, C_5H_5N
g. glycine, $NH_2CH_2CO_2H$
h. ethylamine, $CH_3CH_2NH_2$
i. aniline, $C_6H_5NH_2$
j. dimethylamine, $(CH_3)_2NH$

5. Define each of the following:
a. strong acid
b. strong base
c. weak acid
d. weak base

6. Hydride ion (H^-) and methoxide ion (CH_3O^-) have much greater affinities for H^+ than the OH^- ion does. Write equations for the reactions that occur when NaH and $NaOCH_3$ are dissolved in water.

7. Why is H_3O^+ the strongest acid and OH^- the strongest base that can exist in aqueous solutions?

Autoionization of Water and the pH Scale

8. Give the conditions for a neutral solution at 25°C, in terms of $[H^+]$, pH, and the relationship between $[H^+]$ and $[OH^-]$.

9. Values of K_w as a function of temperature are as follows:

Temp (°C)	K_w
0	1.14×10^{-15}
25	1.00×10^{-14}
35	2.09×10^{-14}
40	2.92×10^{-14}
50	5.47×10^{-14}

a. Is the autoionization of water exothermic or endothermic?
b. What is the pH of pure water at 50°C?
c. Restate your answers to Exercise 8 for water at 50°C. Which of the three criteria for neutrality is most general?
d. From a plot of $\ln(K_w)$ versus $1/T$ (using Kelvin scale) estimate K_w at 37°C, normal physiological temperature.
e. What is the pH of a neutral solution at 37°C?

10. Calculate the pH of each solution:
a. $[H^+] = 1.4 \times 10^{-3}\ M$
b. $[H^+] = 2.5 \times 10^{-10}\ M$
c. $[H^+] = 6.1\ M$
d. $[OH^-] = 3.5 \times 10^{-2}\ M$
e. $[OH^-] = 8 \times 10^{-11}\ M$
f. $[OH^-] = 5.0\ M$
g. pOH = 10.5
h. pOH = 2.3

11. Calculate $[H^+]$ and $[OH^-]$ for each solution:
a. pH = 7.41 (the normal pH of blood)
b. pH = 15.3
c. pH = −1.0
d. pH = 3.2
e. pOH = 5.0
f. pOH = 9.6

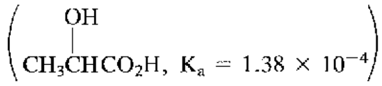
Solutions of Acids

12. Calculate the pH of each of the following solutions of a strong acid in water:
a. $0.1\ M$ HCl
b. $0.1\ M$ HNO_3
c. $0.1\ M$ $HClO_4$
d. $3.0 \times 10^{-5}\ M$ HCl
e. $2.0 \times 10^{-2}\ M$ HNO_3
f. $4.0\ M$ HNO_3

13. Calculate the pH of a $1.0 \times 10^{-12}\ M$ solution of HCl in water. Before checking your answer, decide whether or not it makes sense.

14. A solution is prepared by adding 50.0 mL of concentrated hydrochloric acid and 20.0 mL of concentrated nitric acid to 300 mL of water. Water is added until the final volume is 500.0 mL. Calculate $[H^+]$, $[OH^-]$, and pH for this solution. (See Exercise 2 in Chapter 11 for the composition of the concentrated reagents.)

15. Using the K_a values given in Table 14.2, calculate the concentrations of all species present and the pH for each of the following:
a. $0.20\ M$ $HC_2H_3O_2$
b. $1.5\ M$ HNO_2
c. $0.020\ M$ HF
d. $0.83\ M$ lactic acid



$\left(CH_3CH(OH)CO_2H,\ K_a = 1.38 \times 10^{-4}\right)$

16. Formic acid (HCO_2H) is secreted by ants. Calculate $[H^+]$ and the pH of a $0.025\ M$ solution of formic acid ($K_a = 1.8 \times 10^{-4}$).

17. Calculate the pH of a $0.50\ M$ solution of chlorous acid ($HClO_2$, $K_a = 1.2 \times 10^{-2}$).

18. Boric acid (H_3BO_3) is commonly used in eyewash solutions in chemistry laboratories to neutralize bases splashed in the eye. It acts as a monoprotic acid, but the dissociation reaction is slightly different from that of other acids:

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \qquad K_a = 5.8 \times 10^{-10}$$

Calculate the pH of a $0.50\ M$ solution of boric acid.

19. A solution is prepared by dissolving 0.56 g of benzoic acid ($C_6H_5CO_2H$, $K_a = 6.4 \times 10^{-5}$) in enough water to make 1.0 L of solution. Calculate $[C_6H_5CO_2H]$, $[C_6H_5CO_2^-]$, $[H^+]$, $[OH^-]$, and the pH in this solution.

20. At 25°C a saturated solution of benzoic acid (see Exercise 19) has a pH of 2.8. Calculate the water-solubility of benzoic acid in moles per liter and grams per 100 milliliters.

21. A solution with a volume of 250.0 mL is prepared by diluting 20.0 mL of glacial acetic acid with water. Calculate $[H^-]$ and the pH of this solution. Assume glacial acetic acid is pure liquid acetic acid, with a density of 1.05 g/cm³.

22. Calculate the pH of each of the following:
a. a solution containing $0.10\ M$ HCl and $0.10\ M$ HOCl
b. a solution containing $0.050\ M$ HNO_3 and $0.50\ M$ $HC_2H_3O_2$

23. A solution is prepared by adding 50.0 mL of $0.050\ M$ HCl to 150.0 mL of $0.10\ M$ HNO_3. Calculate the concentrations of all species in this solution.

24. Calculate the pH of a $0.0010\ M$ solution of H_2SO_4.

25. What types of measurements, other than pH measurements, can be made to determine the extent of dissociation of an acid in water?

26. In a 0.100 *M* solution of HF, the percent dissociation is 8.1%. Calculate K_a.

27. Calculate the percent dissociation of the acid in each of the following solutions:
   a. 0.50 *M* acetic acid
   b. 0.050 *M* acetic acid
   c. 0.0050 *M* acetic acid

28. Calculate the percent dissociation of a 0.22 *M* solution of chlorous acid ($HClO_2$) ($K_a = 1.2 \times 10^{-2}$).

29. Using the K_a values in Table 14.2, calculate the percent dissociation in a 0.100 *M* solution of each of the following acids:
   a. hypochlorous acid ($HOCl$)
   b. hydrocyanic acid (HCN)
   c. hydrochloric acid (HCl)

30. The pH of a 0.063 *M* solution of hypobromous acid ($HOBr$ but usually written $HBrO$) is 4.95. Calculate K_a.

31. Trichloroacetic acid (CCl_3CO_2H) is a corrosive acid that is used to precipitate proteins. The pH of a 0.050 *M* solution of trichloroacetic acid is 1.4. Calculate K_a.

32. Using the K_a values in Table 14.4, and only the first dissociation step, calculate the pH of 0.10 *M* solutions of each of the following polyprotic acids:
   a. H_3PO_4
   b. H_3AsO_4
   c. H_2CO_3

33. Calculate $[H^+]$, $[OH^-]$, $[H_3PO_4]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$, and $[PO_4^{3-}]$ for a 0.10 *M* solution of H_3PO_4.

34. Calculate $[CO_3^{2-}]$ in a 0.010 *M* solution of CO_2 in water (H_2CO_3). If all the CO_3^{2-} in this solution comes from the reaction

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

what percent of the H^+ ions in the solution are a result of the dissociation of HCO_3^-? When acid is added to a solution of sodium hydrogen carbonate ($NaHCO_3$), vigorous bubbling occurs. How is this reaction related to the existence of carbonic acid (H_2CO_3) molecules in aqueous solution?

Solutions of Bases

35. Thallium(I) hydroxide is a strong base used in the synthesis of some organic compounds. Calculate the pH of a solution containing 2.48 g of TlOH per liter.

36. Calculate $[OH^-]$, pOH, and pH for each of the following:
   a. 0.25 *M* NaOH
   b. 0.00040 *M* $Ba(OH)_2$
   c. a solution containing 25 g of KOH per liter
   d. a solution containing 150.0 g of NaOH per liter

37. The presence of what element most commonly results in basic properties for an organic compound?

38. Calculate $[OH^-]$, $[H^+]$, and pH of 0.200 *M* solutions of each of the following amines (the missing K_b values are found in Table 14.3):
   a. ethylamine
   b. diethylamine, $(C_2H_5)_2NH$, $K_b = 1.3 \times 10^{-3}$
   c. triethylamine, $(C_2H_5)_3N$, $K_b = 4.0 \times 10^{-4}$
   d. aniline
   e. pyridine
   f. hydroxylamine, $HONH_2$, $K_b = 1.1 \times 10^{-8}$

39. Draw the structures of the conjugate acids of ephedrine and mescaline. See page 586 for structures of the amines.

40. Codeine is a derivative of morphine and is used as an analgesic, narcotic, or antitussive. It was once commonly used in cough syrups, but is now available only by prescription because of its addictive properties. The formula of codeine is $C_{18}H_{21}NO_3$ and the pK_b is 6.05. Calculate the pH of a 10.0-mL solution containing 5.0 mg of codeine.

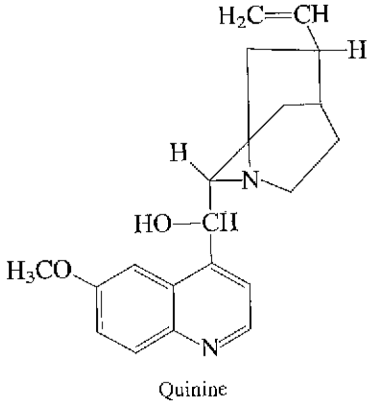
41. What is the percent ionization in each of the following solutions?
   a. 0.10 *M* NH_3
   b. 0.010 *M* NH_3
   c. 0.10 *M* CH_3NH_2

42. For the reaction of hydrazine (N_2H_4) in water,

$$H_2NNH_2 + H_2O \rightarrow H_2NNH_3^+ + OH^-$$

K_b is 3.0×10^{-6}. Calculate the pH of a 2.0 *M* solution of hydrazine in water.

43. Quinine ($C_{20}H_{24}N_2O_2$) is the most important alkaloid derived from cinchona bark. It is used as an antimalarial drug.

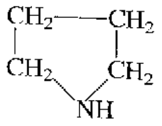


Quinine

For quinine, $pK_{b_1} = 5.1$ and $pK_{b_2} = 9.7$. (Recall that $pK_b = -\log K_b$.) A gram of quinine will dissolve in 1900.0 mL of water. Calculate the pH of a saturated aqueous solution of quinine. Consider only the reaction $Q + H_2O \rightleftharpoons QH^+ + OH^-$ described by pK_{b_1}.

44. The pH of a 0.016 M solution of p-toluidine ($CH_3C_6H_5NH_2$) in water is 8.6. Calculate K_b.

45. The pH of a 1.00×10^{-3} M solution of pyrrolidine is 10.82. Calculate K_b.



Pyrrolidine

Acid-Base Properties of Salts

46. Derive an expression for the relationship between pK_a and pK_b for a conjugate acid-base pair. (Recall that $pK = -\log K$.)

47. Are solutions of the following salts acidic, basic, or neutral? For those that are not neutral, write balanced chemical equations for the reactions causing the solution to be acidic or basic. The relevant K_a and K_b values are found in Tables 14.2 and 14.4.

a. KCl
b. $NaNO_3$
c. $NaNO_2$
d. NH_4NO_3
e. NH_4NO_2
f. $NaHCO_3$
g. $NH_4C_2H_3O_2$
h. NaF

48. Calculate the pH of each of the following solutions:

a. 0.10 M CH_3NH_3Cl
b. 0.050 M NaCN
c. 0.20 M Na_2CO_3 (consider only the reaction $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$)
d. 0.12 M $NaNO_2$
e. 0.45 M NaOCl

49. Is an aqueous solution of $NaHSO_4$ acidic, basic, or neutral? What reaction with water occurs? If solid Na_2CO_3 is added to a solution of $NaHSO_4$, what reaction can occur between the CO_3^{2-} and HSO_4^- ions?

50. Sodium azide (NaN_3) is sometimes added to water to kill bacteria. Calculate the concentration of all species in a 0.010 M solution of NaN_3. The K_a value for hydrazoic acid (HN_3) is 1.9×10^{-5}.

51. Given that the K_a value for acetic acid is 1.8×10^{-5} and the K_a value for hypochlorous acid is 3×10^{-8}, which is the stronger base, OCl^- or $C_2H_3O_2^-$?

Relationships Between Structure and Strengths of Acids and Bases

52. Place the species in each of the following groups in order of increasing acid strength. Give your reason for the particular order you chose in each group.

a. HBrO, $HBrO_2$, $HBrO_3$
b. H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$

53. Place the species in each of the following groups in order of increasing base strength. Give your reasoning in each case.

a. BrO^-, BrO_2^-, BrO_3^-
b. $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}

54. Will the following oxides give acidic, basic, or neutral solutions when dissolved in water? Write reactions to justify your answers.

a. CaO
b. Na_2O
c. SO_2
d. Cl_2O
e. P_4O_{10}
f. NO_2

Lewis Acids and Bases

55. Define each of the following:

a. Arrhenius acid
b. Brönsted-Lowry acid
c. Lewis acid

56. Which of the definitions in Exercise 55 is most general? Write reactions to justify your answer.

57. Identify the Lewis acid and the Lewis base in each of the following reactions:

a. $B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$
b. $Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$
c. $BF_3 + NH_3 \rightleftharpoons F_3BNH_3$
d. $I_2 + I^- \rightleftharpoons I_3^-$
e. $Zn(OH)_2 + 2OH^- \rightleftharpoons Zn(OH)_4^{2-}$

58. Aluminum hydroxide is an amphoteric substance. It can act as either a Brönsted-Lowry base or a Lewis acid. Write a reaction showing $Al(OH)_3$ acting as a base toward H^+ and as an acid toward OH^-.

59. In terms of orbitals and electron arrangements, what must be present for a molecule or ion to act as a Lewis acid? What must be present for a molecule or ion to act as a Lewis base?

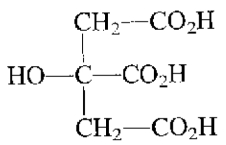
Additional Exercises

60. Liquid ammonia is sometimes used as a solvent for chemical reactions. It undergoes the autoionization reaction:

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

a. What species correspond to H^+ and OH^- in liquid ammonia?
b. What is the condition for a neutral solution in liquid ammonia?
c. Sodium metal reacts with liquid ammonia in a manner analogous to the reaction of sodium metal with water. Write a balanced chemical equation describing this reaction.
d. What advantages might there be to using liquid ammonia as a solvent?

61. Alka-Seltzer employs the reaction between citric acid and sodium bicarbonate to generate its fizz ($CO_2(g)$). The structure of citric acid and values of the acid dissociation constants are



$$\begin{array}{l} \quad\;\; CH_2-CO_2H \\ \quad\;\;\; | \\ HO-C-CO_2H \\ \quad\;\;\; | \\ \quad\;\; CH_2-CO_2H \end{array}$$

$K_{a_1} = 8.4 \times 10^{-4}$

$K_{a_2} = 1.8 \times 10^{-5}$

$K_{a_3} = 4.0 \times 10^{-6}$

Calculate the value of the equilibrium constant for each of the following reactions (we abbreviate citric acid as H_3Cit), using the K_a values for citric acid and for carbonic acid:

$$H_3Cit + HCO_3^- \rightleftharpoons H_2Cit^- + H_2O + CO_2$$
$$H_3Cit + 3HCO_3^- \rightleftharpoons Cit^{3-} + 3H_2O + 3CO_2$$

Hint: When reactions are added, the corresponding equilibrium constants are multiplied.

62. The osmotic pressure of a 1.00×10^{-2} *M* solution of cyanic acid (HOCN) is 217.2 torr at 25°C. Calculate K_a for HOCN from this result.

63. a. The principal equilibrium in a solution of $NaHCO_3$ is

$$HCO_3^- + HCO_3^- \rightleftharpoons H_2CO_3 + CO_3^{2-}$$

Calculate the value of the equilibrium constant for this reaction.
b. At equilibrium, what is the relationship between $[H_2CO_3]$ and $[CO_3^{2-}]$?
c. Using the equilibrium

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$

derive an expression for the pH of the solution in terms of K_{a_1} and K_{a_2} using the result from part b.
d. What is the pH of a solution of $NaHCO_3$?

64. Calculate the value for the equilibrium constant for each of the following reactions:
a. $NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$
b. $NO_2^- + H_3O^+ \rightleftharpoons HNO_2 + H_2O$
c. $NH_4^+ + CH_3CO_2^- \rightleftharpoons NH_3 + CH_3CO_2H$
d. $H_3O^+ + OH^- \rightleftharpoons 2H_2O$
e. $NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$
f. $HNO_2 + OH^- \rightleftharpoons H_2O + NO_2^-$

65. Hemoglobin (abbreviated Hb) is a protein that is responsible for the transport of oxygen in the blood of mammals. Each hemoglobin molecule contains four iron atoms that are the binding sites for O_2 molecules. The oxygen binding is pH dependent. The relevant equilibrium reaction is as follows.

$$HbH_4^{4+} + 4O_2 \rightleftharpoons Hb(O_2)_4 + 4H^+$$

Use Le Châtelier's principle to answer the following.
a. What form of hemoglobin, HbH_4^{4+} or $Hb(O_2)_4$, is favored in the lungs? What form is favored in the cells?
b. When a person hyperventilates, the concentration of CO_2 in the blood is decreased. How does this affect the oxygen-binding equilibrium? How does breathing into a paper bag help to counteract this effect?
c. When a person has suffered a cardiac arrest, injection of a sodium bicarbonate solution is given. Why is this necessary?

66. Construct a thermochemical cycle for the following reaction in terms of bond energies, ionization energies, and electron affinities:

$$HX(g) \rightleftharpoons H^+(g) + X^-(g)$$

a. Calculate ΔH for the above reaction when X = F, Cl, Br, and I.
b. How are the results of this thermochemical cycle consistent with statements in the chapter?

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67. Use the results of Exercise 66 to explain what two things will increase the strength of an acid.

68. Using your conclusions from Exercise 67, place the species in each of the following groups in order of increasing acid strength:

a. H_2O, H_2S, H_2Se (bond energies: H—O, 463 kJ/mol; H—S, 363 kJ/mol; H—Se, 276 kJ/mol)
b. CH_3CO_2H, FCH_2CO_2H, F_2CHCO_2H, F_3CCO_2H
c. NH_4^+, $CH_3NH_3^+$, $HONH_3^+$

Give reasons for the orders you chose.

69. Using your conclusions from Exercise 68, place the species in each of the following groups in order of increasing base strength:

a. OH^-, SH^-, SeH^-
b. NH_3, PH_3 (bond energies: N—H, 386 kJ/mol; P—H, 322 kJ/mol)
c. NH_3, $HONH_2$

70. Calculate the pH of a 1.0×10^{-7} *M* solution of NaOH in water. Consider the amount of hydroxide ion from the autoionization of water and the effect of the added hydroxide ion on the position of the autoionization equilibrium.

71. Making use of the assumptions we ordinarily make in calculating the pH of an aqueous solution of a weak acid, calculate the pH of a 1.0×10^{-6} *M* solution of hypobromous acid (HBrO, $K_a = 2 \times 10^{-9}$). What is wrong with your answer? Why is it wrong? Without trying to solve the problem, tell what has to be included to solve the problem correctly.

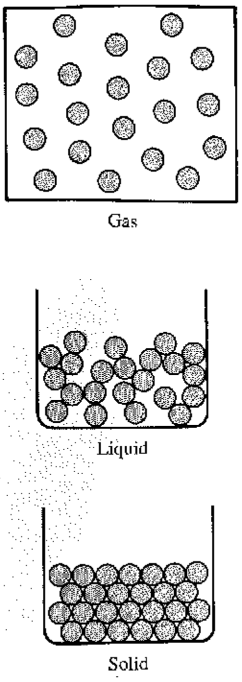


Figure 10.1

Comparison of the three states of matter.

These values show that there is a much greater change in structure in going from the liquid to the gaseous state than in going from the solid to the liquid. This suggests that there are extensive attractive forces among the molecules in liquid water, similar to but not as strong as those in the solid state.

The relative similarity of the liquid and solid states can also be seen in the densities of the three states of water. As shown in Table 10.1, the densities for liquid and solid water are quite close. Compressibilities can also be used to explore the relationship among water's states. At 25°C, the density of liquid water changes from 0.99707 g/cm^3 at a pressure of 1 atm to 1.046 g/cm^3 at 1065 atm. Given the large change in pressure, this is a very small variation in the density. Ice also shows little variation in density with increased pressure. On the other hand, at 400°C, the density of gaseous water changes from 3.26×10^{-3} g/cm^3 at 1 atm pressure to 0.157 g/cm^3 at 242 atm—a huge variation.

The conclusion is clear. The liquid and solid states show many similarities and are strikingly different from the gaseous state (see Fig. 10.1). We must bear this in mind as we develop models for the structures of solids and liquids.

Table 10.1

Densities of the Three States of Water

State	Density (g/cm^3)
Solid (0°C, 1 atm)	0.9168
Liquid (25°C, 1 atm)	0.9971
Gas (400°C, 1 atm)	3.25×10^{-4}

10.1 Intermolecular Forces

PURPOSE

- To define dipole-dipole forces, hydrogen bonding, and London dispersion forces.
- To describe the effects these forces have on the properties of liquids and solids.

Intermolecular forces were introduced in Chapter 5 to explain nonideal gas behavior.

In Chapters 8 and 9 we saw that atoms can form stable units called molecules by sharing electrons. This is called *intramolecular* (within the molecule) bonding. In this chapter we consider the properties of the **condensed states** of matter (liquids and solids) and the forces that cause the aggregation of the components of a substance to form a liquid or a solid. These forces may involve covalent or ionic bonding, or they may involve weaker interactions usually called **intermolecular forces** (because they occur between, rather than within, molecules).

It is important to recognize that when a substance like water changes from solid to liquid to gas, *the molecules remain intact*. The changes of state are due to changes in the forces *among* the molecules rather than those *within* the molecules.

In ice, as we will see later in this chapter, the molecules are virtually locked in place, although they can vibrate about their positions. If energy is added, the motions of the molecules increase, and they eventually achieve the greater movement and disorder characteristic of liquid water. The ice has melted. As more energy is added, the gaseous state is eventually reached, with the individual molecules far apart and interacting relatively little. However, the gas still consists of water molecules. It would take much more energy to overcome the covalent bonds and decompose the water molecules into their component atoms. This can be seen by comparing the energy needed to vaporize 1 mole of liquid water (41.2 kJ) to that needed to break the O—H bonds in 1 mole of water molecules (934 kJ).

Remember that temperature is a measure of the random motions of the particles in a substance.

Dipole—Dipole Forces

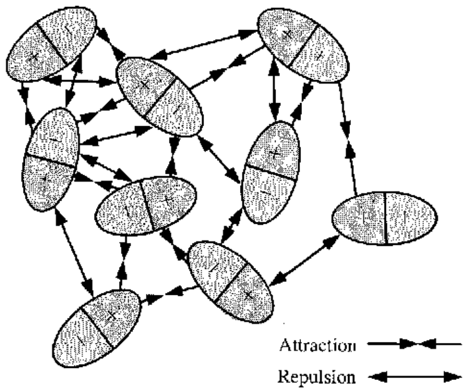
As we saw in Section 8.3, molecules with polar bonds often behave in an electric field as if they had a center of positive charge and a center of negative charge. That is, they exhibit a dipole moment. Molecules with dipole moments can attract each other electrostatically by lining up so that the positive and negative ends are close to each other, as shown in Fig. 10.2(a). This is called a **dipole-dipole attraction.** In a condensed state such as a liquid, the dipoles find the best compromise between attraction and repulsion, as shown in Fig. 10.2(b).

Dipole-dipole forces are typically only about 1% as strong as covalent or ionic bonds, and they rapidly become weaker as the distance between the dipoles increases. At low pressures in the gas phase, where the molecules are far apart, these forces are relatively unimportant.

Particularly strong dipole-dipole forces, however, are seen among molecules in which hydrogen is bound to a highly electronegative atom, such as nitrogen, oxygen, or fluorine. Two factors account for the strengths of these interactions: the great polarity of the bond and the close approach of the dipoles, allowed by the very small size of the hydrogen atom. Because dipole-dipole attractions of this type are so unusually strong, they are given a special name—**hydrogen bonding.** Figure 10.3 shows hydrogen bonding among water molecules.

Hydrogen bonding has a very important effect on various physical properties. For example, the boiling points for the covalent hydrides of the elements in Groups 4A, 5A, 6A, and 7A are given in Fig. 10.4. Note that the nonpolar tetrahedral

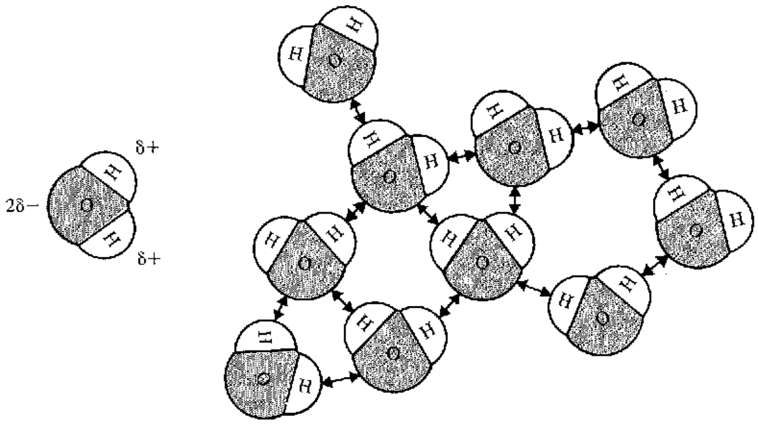
(a)



(b)

Figure 10.2

(a) The electrostatic interaction of two polar molecules. (b) The interaction of many dipoles in a condensed state.



(a)

(b)

Figure 10.3

(a) The polar water molecule. (b) Hydrogen bonding among water molecules. Note that the small size of the hydrogen atoms allows for close interactions.

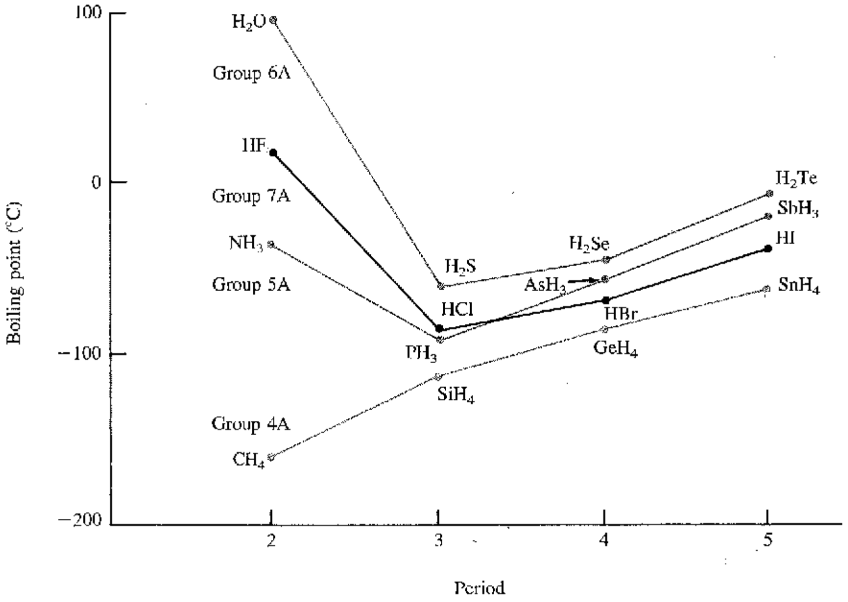


Figure 10.4

The boiling points of the covalent hydrides of elements in Groups 4A, 5A, 6A, and 7A.

hydrides of Group 4A show a steady increase in boiling point with molecular weight (that is, in going down the group), while for the other groups, the lightest member has an unexpectedly high boiling point. Why? The answer lies in the especially large hydrogen-bonding interactions that exist among the smallest molecules with the most polar X—H bonds. An unusually large quantity of energy must therefore be supplied to overcome these interactions and separate the molecules to produce the gaseous state. These molecules will remain together in the liquid state even at high temperatures; hence the very high boiling points.

Boiling point will be defined precisely in Section 10.8.

London Dispersion Forces

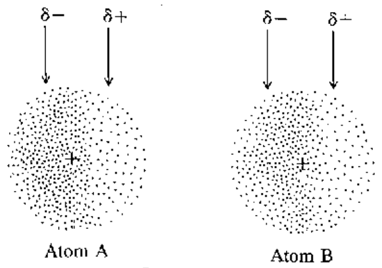
Even molecules without dipole moments must exert forces on each other. We know this because all substances—even the noble gases—exist in the liquid and solid states under certain conditions. The very weak forces that exist among noble gas

Recall from Section 5.7 that, at a given temperature, the velocity of a particle and its mass are inversely related.

atoms and nonpolar molecules are called **London dispersion forces.** To understand the origin of these forces, let us consider a pair of noble gas atoms. Although we usually assume that the electrons of an atom are uniformly distributed about the nucleus, this is apparently not true at every instant. Atoms can develop a momentary nonsymmetrical electron distribution that produces a temporary dipolar arrangement of charge. This *instantaneous dipole* can then *induce* a similar dipole in a neighboring atom, as shown in Fig. 10.5(a). This phenomenon leads to an interatomic attraction that is both weak and short-lived, but significant in the absence of any other types of bonding forces. For these interactions to become strong enough to produce a solid, the motions of the atoms must be greatly slowed down. This explains, for instance, why the noble gas elements have such low freezing points (see Table 10.2).

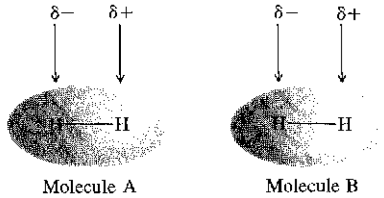
Note from Table 10.2 that the freezing point rises going down the group. There are two principal factors that cause this trend. First, as the atomic mass increases, the average velocity of an atom at a given temperature decreases, allowing the atom to "lock into" the solid more readily. Second, as the atomic number increases, the number of electrons increases, and there is an increased chance of the occurrence of momentary dipole interactions. We say that large atoms with many electrons exhibit a higher *polarizability* than small atoms. Thus the importance of London dispersion forces increases as the size of the atom increases.

These same ideas also apply to nonpolar molecules such as H_2, CH_4, CCl_4, and CO_2 [see Fig. 10.5(b)]. Since none of these molecules has a permanent dipole moment, their principal means of attracting each other is through London dispersion forces.



Instantaneous dipole on A induces a dipole on B.

(a)



Instantaneous dipole on A induces a dipole on B.

(b)

Figure 10.5

(a) An instantaneous polarization can occur on atom A, creating an instantaneous dipole. This dipole creates an induced dipole on neighboring atom B. (b) Nonpolar molecules such as H_2 can develop instantaneous and induced dipoles.

The Freezing Points of the Group 8A Elements

Element	Freezing point (°C)
Helium	−269.7
Neon	−248.6
Argon	−189.4
Krypton	−157.3
Xenon	−111.9

Table 10.2

10.2 The Liquid State

PURPOSE

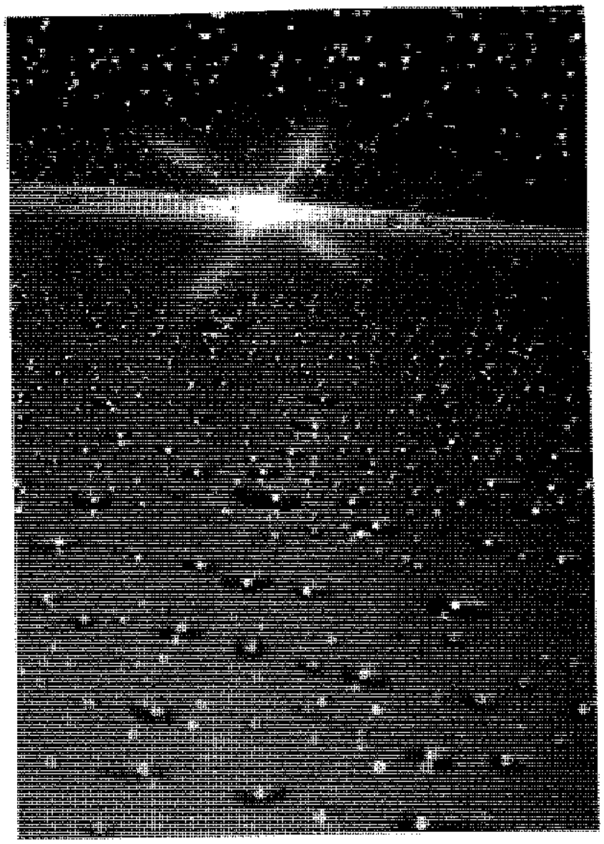
- ☐ To describe some properties of liquids: surface tension, capillary action, and viscosity.

Liquids and liquid solutions are vital to our lives. Of course, water is the most important liquid. Besides being essential to life, it provides a medium for food preparation, for transportation, for cooling in many types of machines and industrial processes, for recreation, for cleaning, and for a myriad of other uses.

Liquids exhibit many characteristics that help us understand their nature. We have already mentioned their low compressibility, lack of rigidity, and high density compared to gases. Many of the properties of liquids give us direct information about the forces that exist among the particles. For example, when a liquid is poured onto a solid surface, it tends to bead as droplets, a phenomenon that depends on the intermolecular forces. Although molecules in the interior of the liquid are completely surrounded by other molecules, those at the liquid surface are subject to attractions only from the side and from below (Fig. 10.6). The effect of this uneven pull on the surface molecules draws them into the body of the liquid and causes a droplet of liquid to assume the shape that has the minimum surface area—a sphere.

For a given volume, a sphere has a smaller surface area than any other shape.

To increase a liquid's surface area, molecules must move from the interior of the liquid to the surface. This requires energy, since some intermolecular forces



Beads of water on a waxed car finish.

must be overcome. The resistance of a liquid to an increase in its surface area is called the **surface tension** of the liquid. As we would expect, liquids with relatively large intermolecular forces tend to have relatively high surface tensions. Thus we can readily predict the surface tension if we know the polarity of the particles comprising the liquid, as seen in Sample Exercise 10.1.

Sample Exercise 10.1

Would you expect liquid carbon tetrachloride (CCl_4) or liquid chloroform ($CHCl_3$) to have the higher surface tension?

Solution

Both carbon tetrachloride and chloroform have molecules with a tetrahedral arrangement of atoms around carbon. However, because chloroform has three bonds of one type and one of another, it has a dipole moment. Carbon tetrachloride, with four equal bonds, does not have a dipole moment. Because of the polar character of its molecules, the much larger intermolecular forces in liquid chloroform cause it to have a higher surface tension.

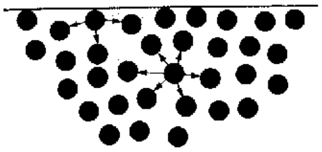


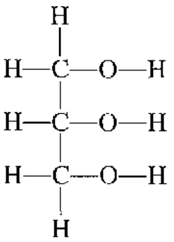
Figure 10.6

A molecule in the interior of a liquid is attracted to the molecules surrounding it, while a molecule at the surface of a liquid is attracted only by molecules below it and on each side. Thus the interior molecules exert a net force pulling the surface molecule into the interior of the liquid.

Polar liquids also exhibit **capillary action,** the spontaneous rising of a liquid in a narrow tube, as shown in Fig. 10.7(a). Two different types of forces are responsible for this property: *cohesive forces,* the intermolecular forces among the molecules of the liquid; and *adhesive forces,* the forces between the liquid molecules and their container. We have already seen how cohesive forces operate among polar molecules. Adhesive forces occur when a container is made of a substance that has polar bonds. For example, glass contains many oxygen atoms with partial negative charges that are attractive to the positive end of a polar molecule such as water. Since water has both strong cohesive (intermolecular) forces and strong adhesive forces to glass, it "pulls itself" up a glass capillary tube (a tube with a small diameter) to a height where the weight of the column of water just balances the water's tendency to be attracted to the glass surface. The concave shape of the meniscus [see Fig. 10.7(a)] shows that water's adhesive forces toward the glass are stronger than its cohesive forces. A nonpolar liquid such as mercury [see Fig. 10.7(b)] shows a lower level in a capillary tube and a convex meniscus. This behavior is characteristic of a liquid in which the cohesive forces are stronger than the adhesive forces toward glass.

The composition of glass is discussed in Section 10.5.

Another property of liquids strongly dependent on intermolecular forces is **viscosity,** a measure of a liquid's resistance to flow. As might be expected, liquids with large intermolecular forces tend to be highly viscous. For example, glycerol, whose structure is



has an unusually high viscosity mainly due to a high capacity to form hydrogen bonds.

Molecular complexity also leads to higher viscosity because very large molecules can become entangled with each other. For example, nonviscous gasoline contains molecules of the type CH_3—$(CH_2)_n$—CH_3, where n varies from about 3 to 8. However, grease, which is very viscous, contains much larger molecules in which n varies from 20 to 25.

In many respects, the development of a structural model for liquids presents greater challenges than developing such a model for the other two states of matter. In the gaseous state, the particles are so far apart and are moving so rapidly that intermolecular forces are negligible under most circumstances. This means we can use a relatively simple model for gases. In the solid state, although the intermolecular forces are large, the molecular motions are minimal and fairly simple models are again possible. The liquid state, however, has both strong intermolecular forces *and* significant molecular motions. Such a situation precludes the use of really simple models for liquids. Recent advances in spectroscopy, the study of the manner in which substances interact with electromagnetic radiation, make it possible to follow the very rapid changes that occur in liquids. As a result, our models of liquids are becoming more accurate. As a starting point, a typical liquid might best be viewed as containing a large number of regions where the arrangements of the components are similar to those found in the solid, but with more disorder, and a smaller number of regions where holes are present. The situation is highly dynamic, with rapid fluctuations occurring in both types of regions.

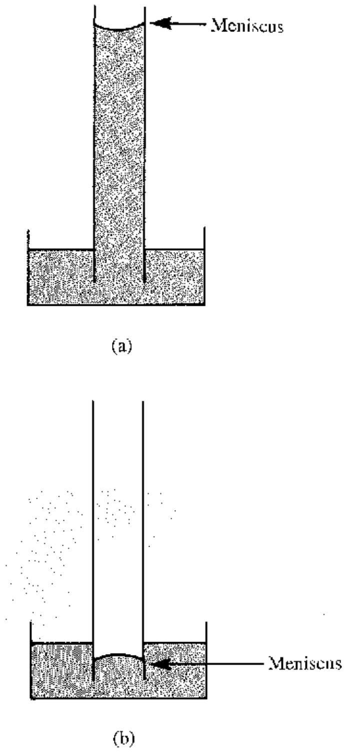


Figure 10.7

(a) The rise of a polar liquid, such as water, in a capillary tube due to large adhesive and cohesive forces. The concave meniscus (the level of the water is higher against the capillary walls than it is in the center of the tube) indicates that the adhesive forces are somewhat larger than the cohesive forces. (b) A nonpolar liquid such as mercury shows a smaller rise than that of water in the capillary tube and a convex meniscus (the mercury level is higher in the center of the tube than it is against the capillary walls). In this case, the cohesive and adhesive forces are both relatively small, but the cohesive force is the larger of the two.

10.3

An Introduction to Structures and Types of Solids

PURPOSE

☐ To contrast crystalline and amorphous solids.

☐ To introduce X-ray diffraction as a means for structure determination.

There are many ways to classify solids, but the broadest categories are **crystalline solids,** those with a highly regular arrangement of their components, and **amorphous solids,** those with considerable disorder in their structure.

The regular arrangement of the components of a crystalline solid at the microscopic level produces the beautiful, characteristic shapes of crystals, such as those shown in Fig. 10.8. The positions of the components in a crystalline solid are usually represented by a **lattice,** a three-dimensional system of points designating the centers of the components (atoms, ions, or molecules). The *smallest repeating unit* of the lattice is called the **unit cell.** Thus a particular lattice can be generated by repeating the unit cell in all three dimensions to form the extended structure. Three common unit cells and their lattices are shown in Fig. 10.9.

Although we will concentrate on crystalline solids in this book, there are many important noncrystalline (amorphous) materials. An example is common glass, which is best pictured as a solution in which the components are "frozen in place" before they can achieve an ordered arrangement. Although glass is a solid (it has a rigid shape), a great deal of disorder exists in its structure.

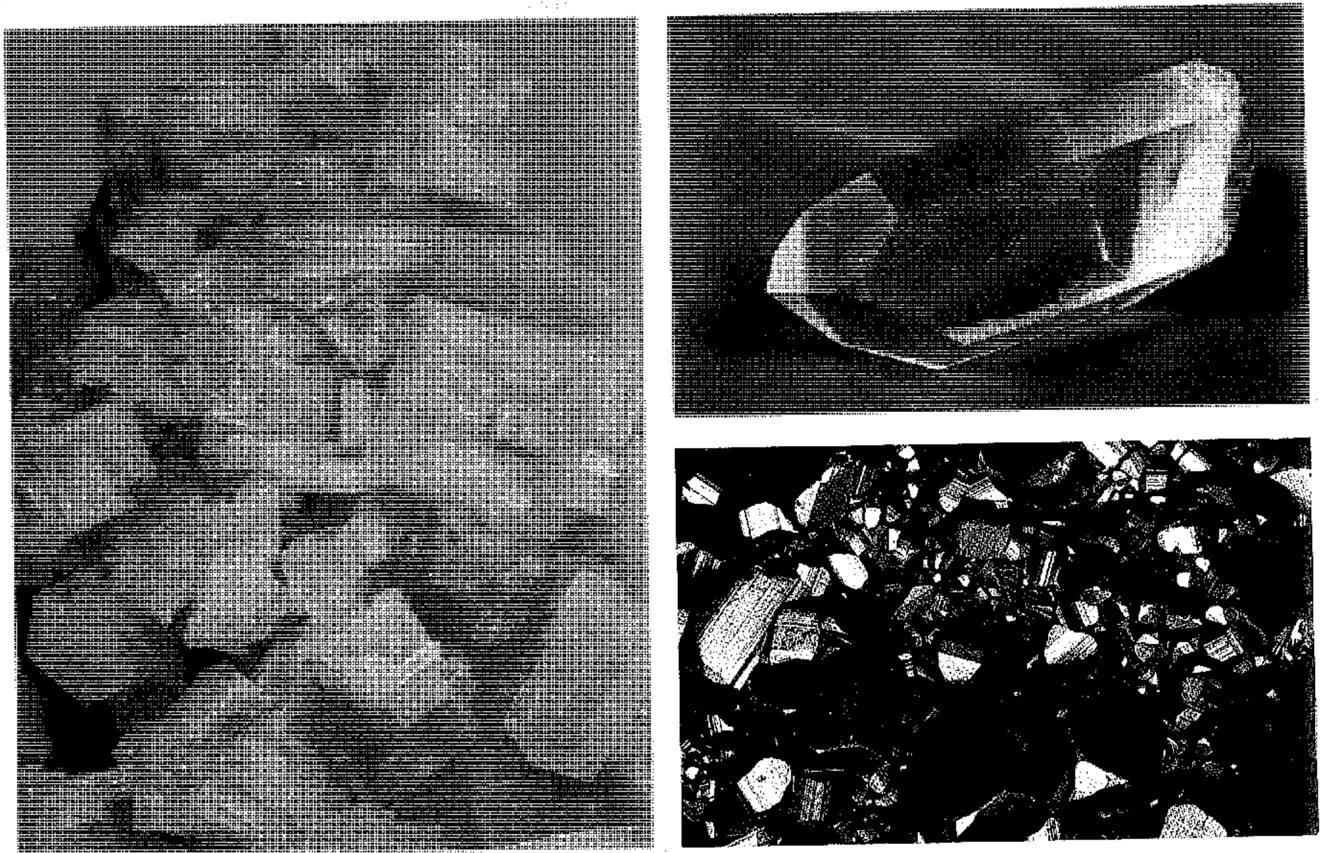


Figure 10.8

Several crystalline solids: (a) halite (NaCl), (b) quartz (SiO_2), and (c) iron pyrite (FeS_2).

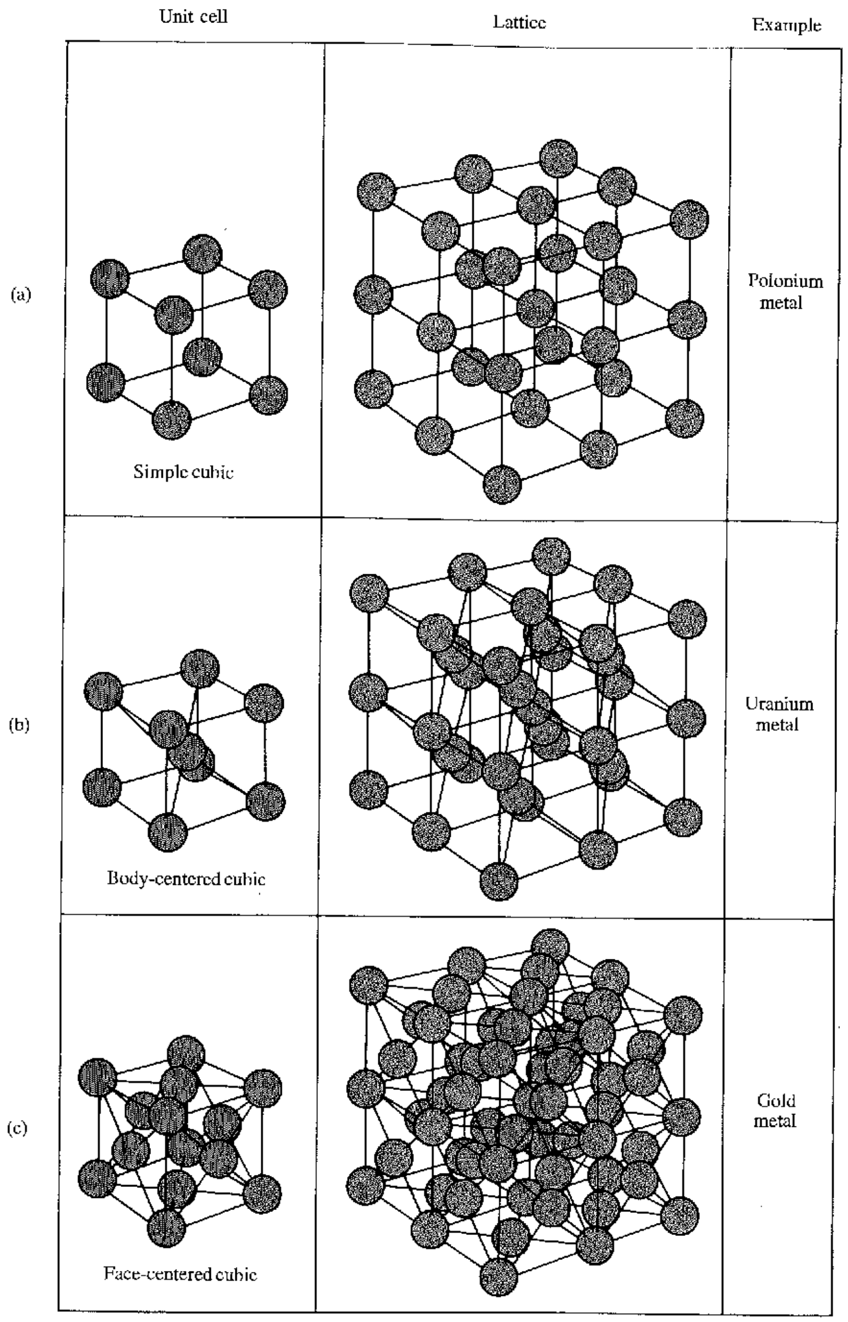


Figure 10.9

Three cubic unit cells and the corresponding lattices: (a) simple cubic, (b) body-centered cubic, and (c) face-centered cubic.

X-ray Analysis of Solids

The structures of crystalline solids are most commonly determined by **X-ray diffraction.** Diffraction occurs when beams of light are scattered from a regular array of points or lines in which the spacings between the components are comparable to the wavelength of the light. Diffraction is due to constructive interference when the waves of parallel beams are in phase and to destructive interference when the waves are out of phase.

Electrons also exhibit diffraction, because they have wavelengths comparable to the spacings in a crystal.

When X rays of a single wavelength are directed at a crystal, a diffraction pattern is obtained, as we saw in Fig. 7.5. The light and dark areas on the photographic plate occur because the waves scattered from various atoms may reinforce or cancel each other when they meet (see Fig. 10.10). The key to whether the waves reinforce or cancel is the difference in distance traveled by the waves after they strike the atoms. The waves are in phase before they are reflected, so if the difference in distance traveled after reflection is an *integral number of wavelengths,* the waves will still be in phase when they meet again.

Since the distance traveled after reflection depends on the distance between the atoms, the diffraction pattern can be used to determine the interatomic spacings. The exact relationship can be worked out using the diagram in Fig. 10.11, which shows two in-phase waves being reflected by atoms in two different layers in a crystal. The extra distance traveled by the lower wave is the sum of the distances xy and yz, and the waves will be in phase after reflection if

$$xy + yz = n\lambda \tag{10.1}$$

Figure 10.10

X rays that are scattered from two different atoms may either (a) reinforce or (b) cancel each other when they meet, depending on whether they are in phase or out of phase.

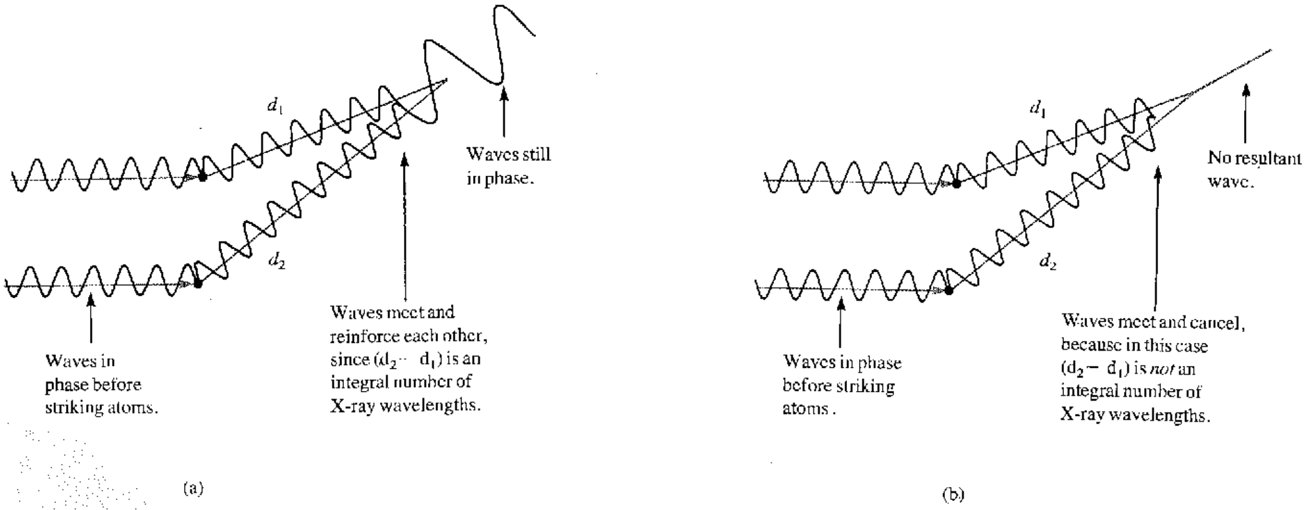
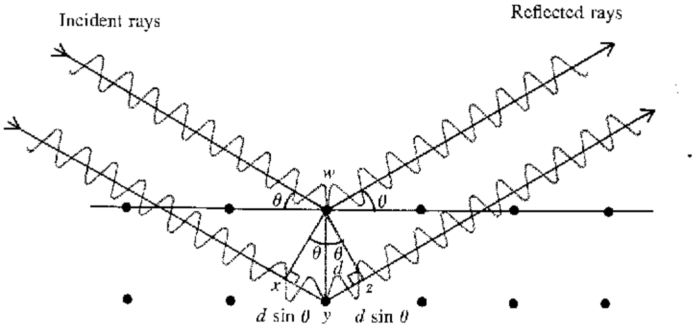


Figure 10.11

Reflection of X rays of wavelength λ from a pair of atoms in two different layers of a crystal. The lower wave travels an extra distance equal to the sum of xy and yz. If this distance is an integral number of wavelengths ($n = 1, 2, 3 \ldots$), the waves will reinforce each other when they exit the crystal.



where n is an integer and λ is the wavelength of the X rays. Using trigonometry (see Fig. 10.14), we can show that

$$xy + yz = 2d \sin \theta \tag{10.2}$$

where d is the distance between the atoms and θ is the angle of incidence and reflection. Combining Equation (10.1) and Equation (10.2) gives

$$n\lambda = 2d \sin \theta \tag{10.3}$$

Equation (10.3) is called the **Bragg equation** after William Henry Bragg (1862–1942) and his son William Lawrence Bragg (1890–1972), who shared the Nobel prize in physics in 1915 for their pioneering work in X-ray crystallography.

A diffractometer is a computer-controlled instrument used for carrying out the X-ray analysis of crystals. It rotates the crystal with respect to the X-ray beam and collects the data produced by the scattering of the X rays from the various planes of atoms in the crystal. The results are then analyzed by computer. The techniques for crystal structure analysis have reached a level of sophistication that allows the determination of very complex structures, such as those important in biological systems. Using X-ray diffraction, we can gather data on bond lengths and angles, and in doing so can test the predictions of our models of molecular geometry.

Sample Exercise 10.2

X rays of wavelength 1.54 Å were used to analyze an aluminum crystal. A reflection was produced at $\theta = 19.3°$. Assuming $n = 1$, calculate the distance d between the planes of atoms producing this reflection.

Solution

To determine the distance between the planes, we use Equation (10.3) with $n = 1$, $\lambda = 1.54$ Å, and $\theta = 19.3°$. Since $2d \sin \theta = n$,

$$d = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(1.54\ \text{Å})}{(2)(0.3305)} = 2.33\ \text{Å}$$

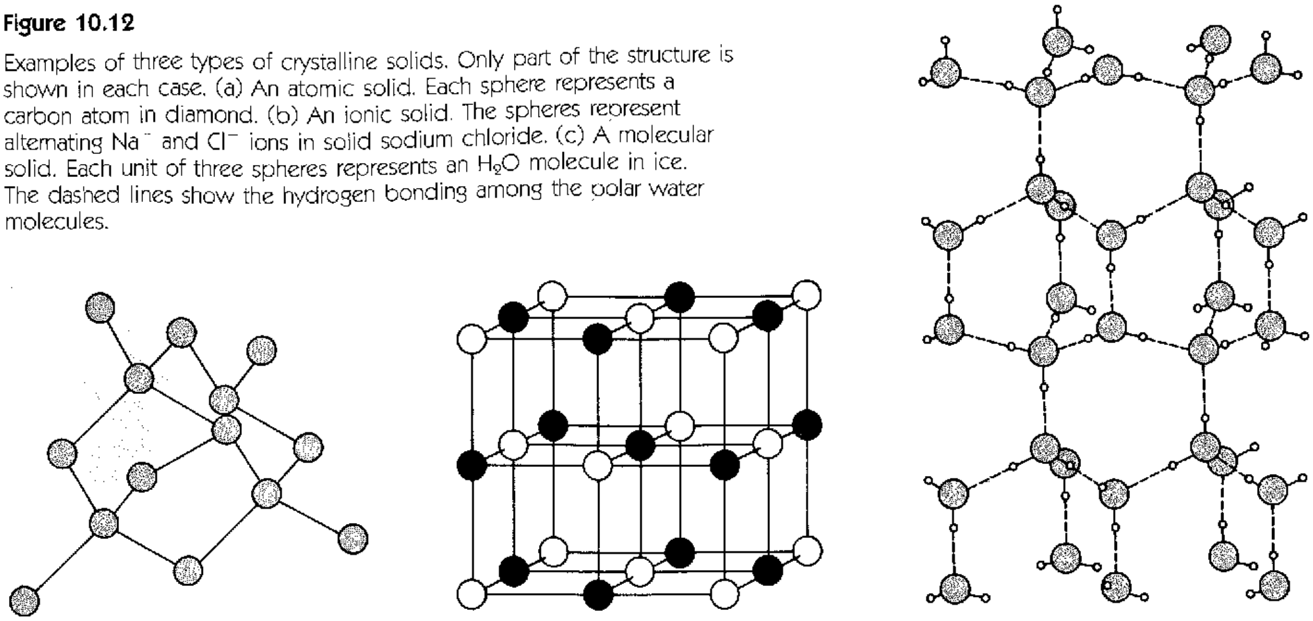
Types of Crystalline Solids

There are many different types of crystalline solids. For example, although both sugar and salt dissolve readily in water, the properties of the resulting solutions are quite different. The salt solution readily conducts an electric current, while the sugar solution does not. This behavior arises from the nature of the components in these two solids. Common salt (NaCl) is an ionic solid; it contains Na^+ and Cl^- ions. When solid sodium chloride dissolves in the polar water, sodium and chloride ions are distributed throughout the resulting solution and are free to conduct electrical current. Table sugar (sucrose), on the other hand, is composed of neutral molecules that are dispersed throughout the water when the solid dissolves. No ions are present, and the resulting solution does not conduct electricity. These examples illustrate two important types of solids: **ionic solids,** represented by sodium chloride; and **molecular solids,** represented by sucrose.

A third type of solid is represented by elements such as graphite and diamond (both pure carbon), boron, silicon, and all metals. These substances all contain atoms covalently bonded to each other; we will call them **atomic solids.** Examples of the three types of solids are shown in Fig. 10.12.

Figure 10.12

Examples of three types of crystalline solids. Only part of the structure is shown in each case. (a) An atomic solid. Each sphere represents a carbon atom in diamond. (b) An ionic solid. The spheres represent alternating Na^+ and Cl^- ions in solid sodium chloride. (c) A molecular solid. Each unit of three spheres represents an H_2O molecule in ice. The dashed lines show the hydrogen bonding among the polar water molecules.



Diamond

(a)

Sodium chloride

(b)

Ice

(c)

The internal forces in a solid determine the properties of the solid.

The properties of a solid are determined primarily by the nature of the forces that hold the solid together. For example, although argon, copper, and diamond all form atomic solids, they have strikingly different properties. Argon has a very low melting point (−189°C), while diamond and copper melt at high temperatures (about 3500°C and 1083°C, respectively). Copper is an excellent conductor of electricity, while argon and diamond are both insulators. Copper can be easily changed in shape; it is both malleable (will form thin sheets) and ductile (can be pulled into a wire). Diamond, on the other hand, is the hardest natural substance known. The marked differences in properties among these three atomic solids are due to bonding differences. We will explore the bonding in solids in the next two sections.

10.4 Structure and Bonding in Metals

PURPOSE

☐ To discuss the concept of closest packing of metal atoms.
☐ To describe two models for bonding in metals.
☐ To define and classify alloys.

Metals are characterized by high thermal and electrical conductivity, malleability, and ductility. As we will see, these properties can be traced to the nondirectional covalent bonding found in metallic crystals.

The closest packing model for metallic crystals assumes that metal atoms are uniform, hard spheres.

A metallic crystal can be pictured as containing spherical atoms packed together and bonded to each other equally in all directions. We can model such a structure by packing uniform, hard spheres in a manner that most efficiently uses the available space. Such an arrangement is called **closest packing.** The spheres are packed in layers, as shown in Fig. 10.13(a), where each sphere is surrounded by six others. In the second layer the spheres do not lie directly over those in the first layer. Instead each one occupies an indentation (or dimple) formed by three spheres in the first layer [see Fig. 10.13(b)]. In the third layer the spheres can occupy the dimples of the second layer in two possible ways. They can occupy positions so that each sphere in the third layer lies directly over a sphere in the first layer (the *aba* arrangement), or they can occupy positions so that no sphere in the third layer lies over one in the first layer (the *abc* arrangement).

The *aba* arrangement has the *hexagonal* unit cell shown in Fig. 10.14, and the resulting structure is called the **hexagonal closest packed (hcp) structure.** The *abc* arrangement has a *face-centered cubic* unit cell, as shown in Fig. 10.15, and the resulting structure is called the **cubic closest packed (ccp) structure.** Note that in the hcp structure the spheres in every other layer occupy the same vertical position (*ababab* . . .), while in the ccp structure the spheres in every fourth layer occupy the same vertical position (*abcabca* . . .). A characteristic of both structures is that each sphere has 12 equivalent nearest neighbors: 6 in the same layer, 3 in the layer above, and 3 in the layer below (that form the dimples). This is illustrated for the hcp structure in Fig. 10.16 on the following page.

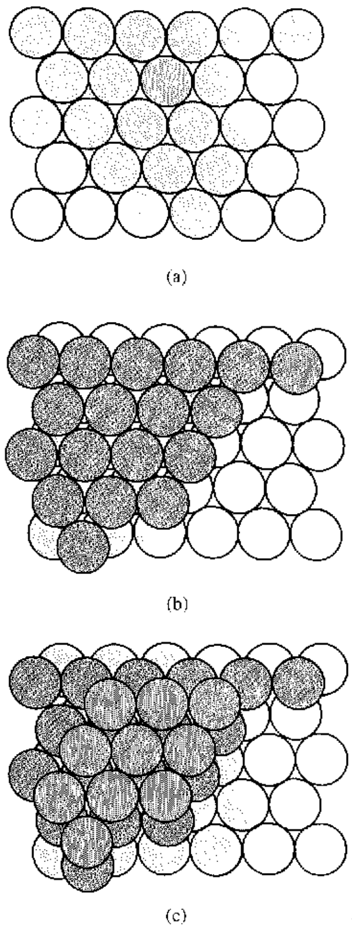
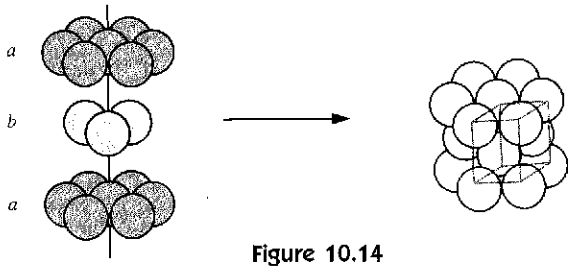


Figure 10.13

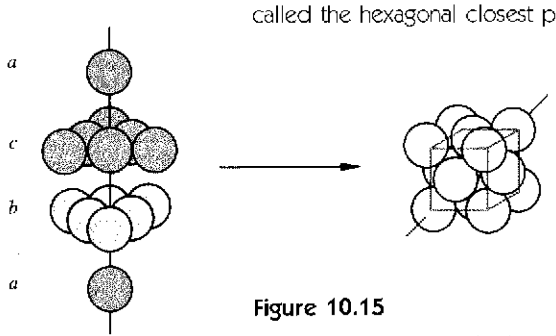
The closest packing arrangement of uniform spheres. (a) A typical layer where each sphere is surrounded by six others. (b) The second layer is like the first, but it is displaced so that each sphere in the second layer occupies a dimple in the first layer. (c) The spheres in the third layer can occupy dimples in the second so that the spheres in the third layer lie directly over those in the first layer (*aba*), or they can occupy dimples in the second layer so that no spheres in the third layer lie above any in the first layer (*abc*).



Atom in third layer lies over atom in first layer.

Figure 10.14

When spheres are closest packed so that the spheres in the third layer are directly over those in the first layer (*aba*), the unit cell is the hexagonal prism illustrated here. Because of its hexagonal unit cell, the *aba* arrangement is called the hexagonal closest packed structure.



An atom in every fourth layer lies over an atom in the first layer.

Figure 10.15

When spheres are packed in the *abc* arrangement, the unit cell is face-centered cubic. To make the cubic arrangement easier to see, the vertical axis has been tilted as shown. Since this arrangement has a cubic unit cell, it is called the cubic closest packed structure.

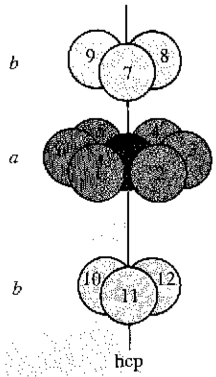
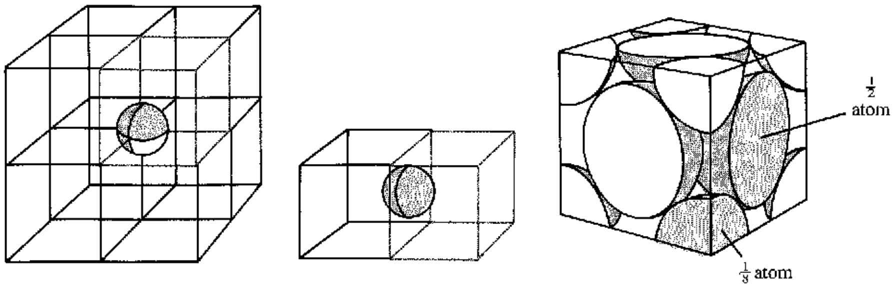


Figure 10.16

The indicated sphere has 12 nearest neighbors—6 in the same layer, 3 in the layer above, and 3 in the layer below, the latter 6 forming the dimples above and below the sphere.

Knowing the *net* number of spheres (atoms) in a particular unit cell is important for many applications involving solids. To illustrate how to find the net number of spheres in a unit cell, we will consider a face-centered cubic unit cell (Fig. 10.17). Note that this unit cell is defined by the *centers* of the spheres on the cube's corners. Thus 8 cubes share a given sphere, so $\frac{1}{8}$ of this sphere lies inside each unit cell. Since a cube has 8 corners, there are $8 \times \frac{1}{8}$ pieces, or enough to put together 1 whole sphere. The spheres at the center of each face are shared by 2 unit cells, so $\frac{1}{2}$ of each lies inside a particular unit cell. Since the cube has 6 faces, we have $6 \times \frac{1}{2}$ pieces, or enough to construct 3 whole spheres. Thus the net number of spheres in a face-centered cubic unit cell is

$$\left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$$



(a) (b) (c)

Figure 10.17

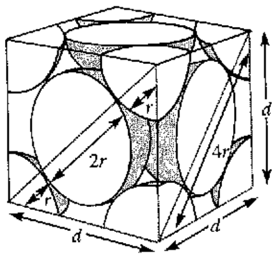
The net number of spheres in a face-centered cubic unit cell. (a) Note that the sphere on a corner of the colored cell is shared with 7 other unit cells. Thus $\frac{1}{8}$ of such a sphere lies within a given unit cell. Since there are 8 corners in a cube, there are 8 of these $\frac{1}{8}$ pieces, or 1 net sphere. (b) The sphere on the center of each face is shared by two unit cells, and thus each unit cell has $\frac{1}{2}$ of each of these types of spheres. There are 6 of these $\frac{1}{2}$ spheres to give 3 net spheres. (c) Thus the face-centered cubic unit cell contains 4 net spheres.

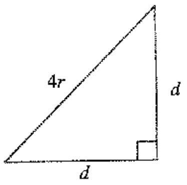
Sample Exercise 10.3

Silver crystallizes in a cubic closest packed structure. The radius of a silver atom is 1.44 Å. Calculate the density of solid silver.

Solution

Density is mass per unit volume. Thus we need to know how many silver atoms occupy a given volume in the crystal. The structure is cubic closest packed, which means the unit cell is face-centered cubic, as shown in the accompanying figure.





We must find the volume of this unit cell for silver and the net number of atoms it contains. Note that in this structure the atoms touch along the diagonals of each face and not along the edges of the cube. Thus the length of the diagonal is $r + 2r + r$, or $4r$. We use this fact to find the length of the edge of the cube by the Pythagorean theorem:

$$\begin{aligned} d^2 + d^2 &= (4r)^2 \\ 2d^2 &= 16r^2 \\ d^2 &= 8r^2 \\ d &= \sqrt{8r^2} = r\sqrt{8} \end{aligned}$$

Since $r = 1.44$ Å for a silver atom,

$$d = (1.44\ \text{Å})(\sqrt{8}) = 4.07\ \text{Å}$$

The volume of the unit cell is d^3, which is $(4.07\ \text{Å})^3$, or $67.4\ \text{Å}^3$. We convert this to cubic centimeters as follows:

$$67.4\ \text{Å}^3 \times \left(\frac{1.00 \times 10^{-8}\ \text{cm}}{\text{Å}}\right)^3 = 6.74 \times 10^{-23}\ \text{cm}^3$$

Since we know that the net number of atoms in the face-centered cubic unit cell is 4, we have 4 silver atoms contained in a volume of $6.74 \times 10^{-23}\ \text{cm}^3$. The density is therefore

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{(4\ \text{atoms})(107.9\ \text{g/mol})(1\ \text{mol}/6.022 \times 10^{23}\ \text{atoms})}{6.74 \times 10^{-23}\ \text{cm}^3}$$

$$= 10.6\ \text{g/cm}^3$$

Examples of metals that are cubic closest packed are aluminum, iron, copper, cobalt, and nickel. Magnesium and zinc are hexagonal closest packed. Calcium and certain other metals can crystallize in either of these structures. Some metals, however, assume structures that are not closest packed. For example, the alkali metals have structures characterized by a *body-centered cubic (bcc) unit cell* [see Fig. 10.10(b)], where the spheres touch along the body diagonal of the cube. In this structure each sphere has 8 nearest neighbors (count the number of atoms around the atom at the center of the unit cell), as compared to 12 in the closest packed structures. Why a particular metal adopts the structure it does is not well understood.

Bonding in Metals

Any successful bonding model for metals must account for the typical physical properties of metals: malleability, ductility, and the efficient and uniform conduction of heat and electricity in all directions. Although the shapes of most pure metals can be changed relatively easily, most metals are durable and have high melting points. These facts indicate that the bonding in most metals is both *strong* and *nondirectional*. That is, although it is difficult to separate metal atoms, it is relatively easy to move them, provided the atoms stay in contact with each other.

The simplest picture that explains these observations is the **electron sea model,** which envisions a regular array of metal cations in a "sea" of valence electrons (see Fig. 10.18). The mobile electrons can conduct heat and electricity, and the cations can be easily moved around as the metal is hammered into a sheet or pulled into a wire.

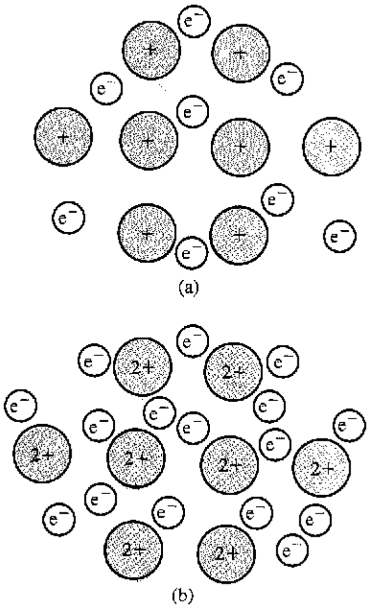


Figure 10.18

The electron sea model for metals postulates a regular array of cations in a "sea" of valence electrons. (a) Representation of an alkali metal (Group 1A) with one valence electron. (b) Representation of an alkaline earth metal (Group 2A) with two valence electrons.

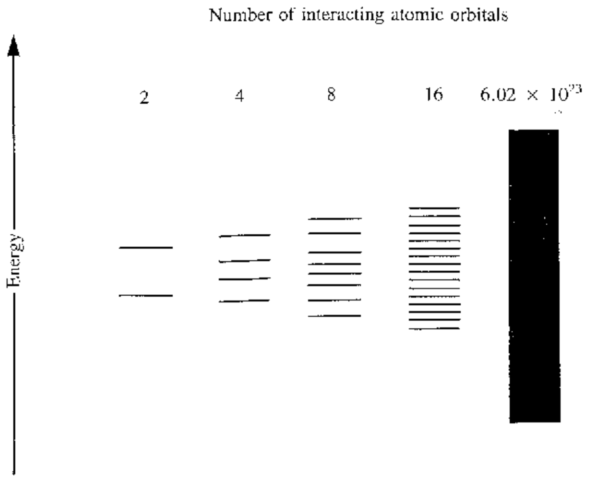


Figure 10.19

The molecular orbital energy levels produced when various numbers of atomic orbitals interact. Note that for two atomic orbitals two rather widely spaced energy levels result. (Recall the description of H_2 in Section 9.2.) As more atomic orbitals are available to form molecular orbitals, the resulting energy levels are more closely spaced, finally producing a band of very closely spaced orbitals.

A related model that gives a more detailed view of the electron energies and motions is the **band model,** or molecular orbital (MO) model, for metals. In this model the electrons are assumed to travel around the metal crystal in molecular orbitals formed from the valence atomic orbitals of the metal atoms (Fig. 10.19).

The MO model is applied to Li_2 in Section 9.3.

Recall that in the MO model for the gaseous Li_2 molecule, two widely spaced molecular orbital energy levels (bonding and antibonding) result when two identical atomic orbitals interact. However, when many metal atoms interact, as in a metal crystal, the large number of resulting molecular orbitals become more closely spaced and finally form a virtual continuum of levels, called **bands,** as shown in Fig. 10.19.

As an illustration, picture a magnesium metal crystal, which has an hcp structure. Since each magnesium atom has one $3s$ and three $3p$ valence atomic orbitals, a crystal with n magnesium atoms has available $n(3s)$ and $3n(3p)$ orbitals to form the molecular orbitals, as illustrated in Fig. 10.20. Note that the core electrons are localized, as shown by their presence in the energy "well" around each magnesium atom. However, the valence electrons occupy closely spaced molecular orbitals, which are only partially filled.

The existence of empty molecular orbitals close in energy to filled molecular orbitals explains the thermal and electrical conductivity of metal crystals. Metals conduct electricity and heat very efficiently because of the availability of highly mobile electrons. For example, when an electrical potential is placed across a strip of metal, for current to flow electrons must be free to move from the negative to the positive areas of the metal. In the band model for metals, mobile electrons are furnished when electrons in filled molecular orbitals are excited into empty ones. These conduction electrons are free to travel throughout the metal crystal as dictated by the potential imposed on the metal. The molecular orbitals occupied by these conducting electrons are called **conduction bands.** These mobile electrons also account for the efficiency of the conduction of heat through metals. When one end of a metal rod is heated, the mobile electrons can rapidly transmit the thermal energy to the other end.

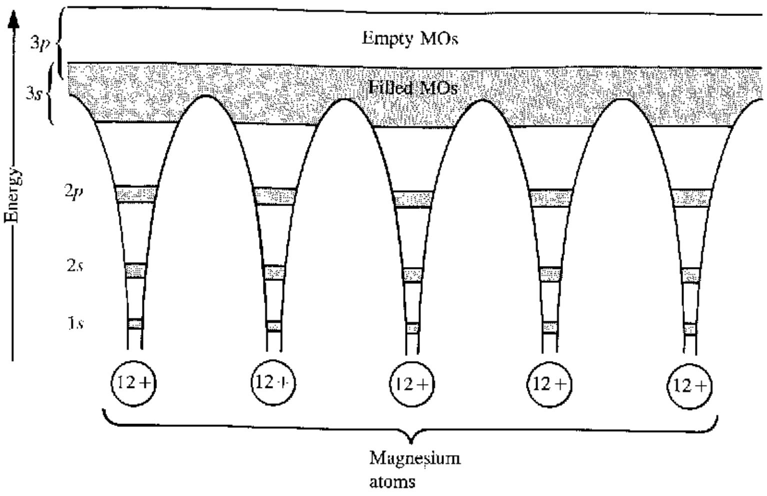


Figure 10.20

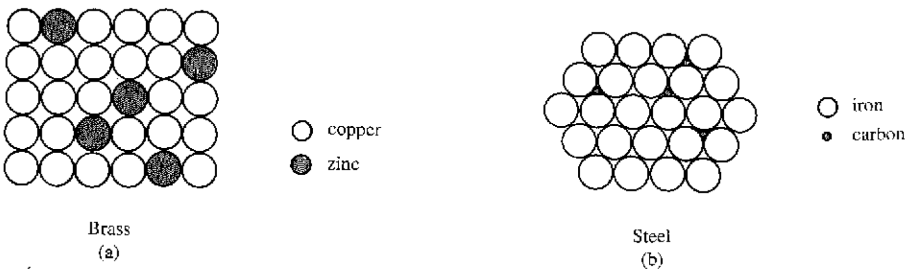
A representation of the energy levels (bonds) in a magnesium crystal. The electrons in the 1*s*, 2*s*, and 2*p* orbitals are close to the nuclei and thus are localized on each magnesium atom as shown. However, the 3*s* and 3*p* valence orbitals overlap and mix to form molecular orbitals. Electrons in these energy levels can travel throughout the crystal.

Metal Alloys

Because of the nature of the structure and bonding of metals, other elements can be introduced into a metallic crystal relatively easily to produce substances called alloys. An **alloy** is best defined as *a substance that contains a mixture of elements and has metallic properties*. Alloys can be conveniently classified into two types.

In a **substitutional alloy** some of the host metal atoms are *replaced* by other metal atoms of similar size. For example, in brass approximately one-third of the atoms in the host copper metal have been replaced by zinc atoms, as shown in Fig. 10.21(a). Sterling silver (93% silver and 7% copper), pewter (85% tin, 7% copper, 6% bismuth and 2% antimony), and plumber's solder (67% lead and 33% tin) are other examples of substitutional alloys.

An **interstitial alloy** is formed when some of the interstices (holes) in the closest packed metal structure are occupied by small atoms, as shown in Fig. 10.21(b). Steel, the best known interstitial alloy, contains carbon atoms in the holes of an iron crystal. The presence of the interstitial atoms changes the properties of the host metal. Pure iron is relatively soft, ductile, and malleable due to the absence of strong directional bonding. The spherical metal atoms can be rather easily moved with respect to each other. However, when carbon, which forms strong directional bonds, is introduced into an iron crystal, the presence of the directional carbon-iron bonds makes the resulting alloy harder, stronger, and less ductile than pure iron. The amount of carbon directly affects the properties of steel. *Mild steels*, containing less than 0.2% carbon, are ductile and malleable and used for nails, cables, and



Brass
(a)

Steel
(b)

Figure 10.21

Two types of alloys. (a) Brass is a substitutional alloy in which copper atoms in the host crystal are replaced by similarly sized zinc atoms.
(b) Steel is an interstitial alloy in which carbon atoms occupy interstices (holes) among the closest packed iron atoms.

chains. *Medium steels*, containing 0.2–0.6% carbon, are harder than mild steels and are used in rails and structural steel beams. *High-carbon steels*, containing 0.6–1.5% carbon, are tough and hard and are used for springs, tools, and cutlery.

The manufacture of steel will be discussed in detail in Chapter 24.

Many types of steel also contain elements in addition to iron and carbon. Such steels are often called *alloy steels* and can be viewed as being mixed interstitial (carbon) and substitutional (other metals) alloys. Bicycle frames, for example, are constructed from a wide variety of alloy steels. The compositions of the two brands of steel tubing most commonly used in expensive racing bicycles are given in Table 10.3.

The Composition of the Two Brands of Steel Tubing Most Commonly Used to Make Lightweight Racing Bicycles

Brand of tubing	% C	% Si	% Mn	% Mo	%Cr
Reynolds	0.25	0.25	1.3	0.20	—
Columbus	0.25	0.30	0.65	0.20	1.0

Table 10.3

10.5 Carbon and Silicon: Network Atomic Solids

PURPOSE

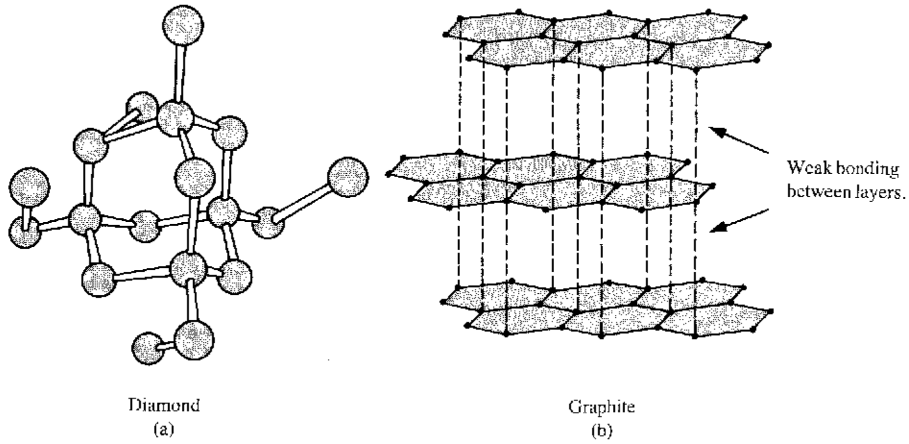
- ☐ To show how the bonding in elemental carbon and silicon accounts for the widely different properties of their compounds.
- ☐ To explain how a semiconductor works.

Many atomic solids contain strong directional covalent bonds. We will call these substances **network solids.** In contrast to metals, these materials are typically brittle and do not efficiently conduct heat or electricity. To illustrate network solids, in this section we will discuss two very important elements, carbon and silicon, and some of their compounds.

Different forms of a given element are called allotropes.

Carbon, which occurs in the *allotropes* diamond and graphite, is a typical network solid. In diamond, the hardest naturally occurring substance, each carbon atom is surrounded by a tetrahedral arrangement of other carbon atoms, as shown in Fig. 10.22(a). This structure is stabilized by covalent bonds, which, in terms of the localized electron model, are formed by the overlap of sp^3 hybridized carbon atomic orbitals.

It is also useful to consider the bonding among the carbon atoms in diamond in terms of the molecular orbital model. Energy-level diagrams for diamond and a typical metal are given in Fig. 10.23. Recall that the conductivity of metals can be explained by postulating that electrons are excited from filled levels into the very near empty levels, or conduction bands. However, note that in the energy-level diagram for diamond there is *a large gap between the filled and the empty levels.* This means that electrons cannot be easily transferred to the empty conduction bands. As a result, diamond is not expected to be a good electrical conductor. In fact, this prediction of the model agrees exactly with the observed behavior of diamond, which is known to be an electrical *insulator*—it does not conduct an electrical current.



Diamond
(a)

Graphite
(b)

Figure 10.22

The structure of the carbon allotropes. (a) Diamond contains a network of carbon atoms, each of which is bonded to four other carbon atoms in a tetrahedral arrangement. (b) Graphite contains layers of carbon atoms organized in fused six-membered rings.

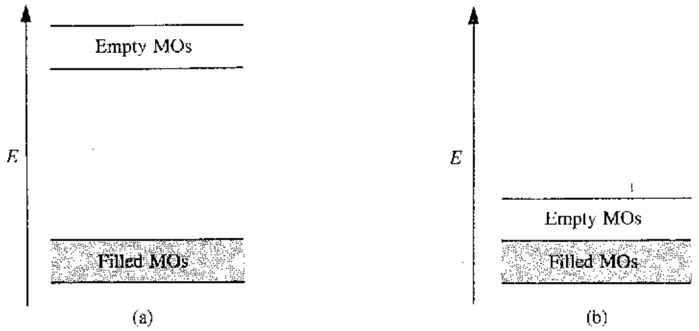


Figure 10.23

Partial representation of the molecular orbital energies in (a) diamond and (b) a typical metal. Note that in the metal the filled and empty levels are adjacent, but in diamond there is a large gap between the filled and empty levels.

Graphite, the other allotrope of elemental carbon, is very different from diamond. While diamond is hard, basically colorless, and an insulator, graphite is slippery, black, and a conductor. These differences, of course, arise from the differences in bonding in the two types of solids. In contrast to the tetrahedral arrangement of carbon atoms in diamond, the structure of graphite is based on layers of carbon atoms arranged in fused six-membered rings, as shown in Fig. 10.22(b). Each carbon atom in a particular layer of graphite is surrounded by three other carbon atoms in a trigonal planar arrangement with 120° bond angles. The localized electron model predicts sp^2 hybridization in this case. The three sp^2 orbitals on each carbon are used to form σ bonds to three other carbon atoms. One $2p$ orbital remains unhybridized on each carbon and is perpendicular to the plane of carbon atoms, as shown in Fig. 10.24. These orbitals combine to form a group of closely spaced π

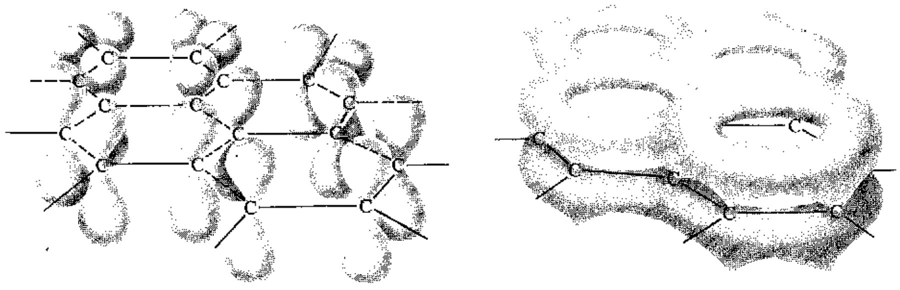


Figure 10.24

The p orbitals perpendicular to the plane of the carbon ring system in graphite can combine to form an extensive π-bonding network.

molecular orbitals that are important in two ways. First, they contribute significantly to the stability of the graphite layers because of the π bond formation. Second, the π molecular orbitals with their delocalized electrons account for the electrical conductivity of graphite. These closely spaced orbitals are exactly analogous to the conduction bands found in metal crystals.

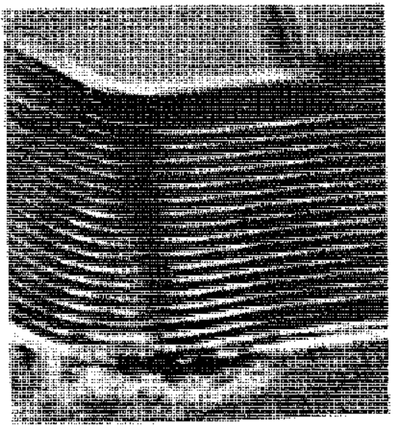


Figure 10.25

Electron microscopic view of graphite.

Graphite is often used as a lubricant in locks (where oil is undesirable because it collects dirt). The slipperiness that is characteristic of graphite can be explained by noting that graphite has very strong bonding *within* the layers of carbon atoms but little bonding *between* the layers (the valence electrons are all used to form σ and π bonds among carbons within the layers). This arrangement allows the layers to slide past one another quite readily. Graphite's layered structure is quite obvious when viewed with a high-magnification electron microscope (Fig. 10.25). This is in contrast to diamond which has uniform bonding in all directions in the crystal.

Because of their extreme hardness, diamonds are extensively used in industrial cutting implements. Thus it is desirable to convert cheaper graphite to diamond. As we might expect from the higher density of diamond (3.5 g/cm^3) compared to that of graphite (2.2 g/cm^3), this transformation can be accomplished by applying very high pressures to graphite. The application of 150,000 atm of pressure at 2800°C converts graphite virtually completely to diamond. The high temperature is required to break the strong bonds in graphite so the rearrangement can occur.

Silicon is an important constituent of the compounds that make up the earth's crust. In fact, silicon is to geology as carbon is to biology. Just as carbon compounds are the basis for most biologically significant systems, silicon compounds are fundamental to most of the rocks, sands, and soils found in the earth's crust. However, although carbon and silicon are next to each other in Group 4A of the periodic table, the carbon-based compounds of biology and the silicon-based compounds of geology have markedly different structures. Carbon compounds typically contain long strings of carbon-carbon bonds, while the most stable silicon compounds involve chains with silicon-oxygen bonds. The *most important silicon compounds contain silicon and oxygen.*

The fundamental silicon-oxygen compound is **silica,** which has the empirical formula SiO_2. Knowing the properties of the similar compound carbon dioxide, one might expect silica to be a gas that contains discrete SiO_2 molecules. In fact, nothing could be further from the truth—quartz and some types of sand are typical of the materials composed of silica. What accounts for this difference? The answer lies in the bonding.

Recall that the Lewis structure for CO_2 is

$$:\!\dot{\underset{\cdot}{O}}=C=\dot{\underset{\cdot}{O}}\!:$$

and that each C=O bond is a combination of a σ bond, involving a carbon *sp* hybrid orbital, and a π bond, involving a carbon 2*p* orbital. On the contrary, silicon cannot use its valence 3*p* orbitals to form strong π bonds to oxygen, mainly because of the larger size of the silicon atom and its orbitals, which results in less effective overlap with the smaller oxygen orbitals. Therefore, instead of forming π bonds, the silicon atom satisfies the octet rule by forming single bonds to four oxygen atoms, as shown in the representation of the structure of quartz in Fig. 10.26. Note that each silicon atom is at the center of a tetrahedral arrangement of oxygen atoms, which are shared with other silicon atoms. Although the empirical formula for quartz is SiO_2, the structure is based on a *network* of SiO_4 tetrahedra with shared oxygen atoms rather than discrete SiO_2 molecules. It is obvious that the differing

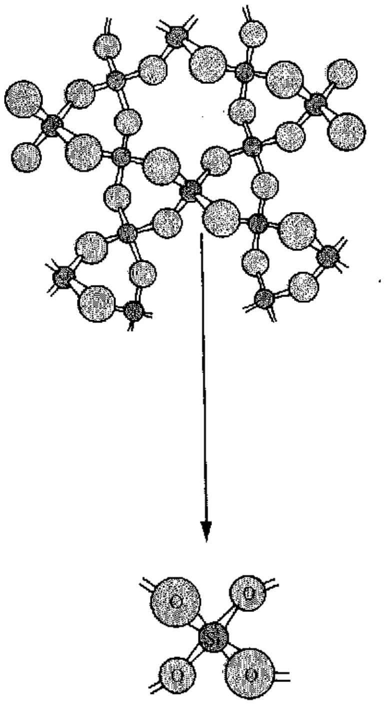


Figure 10.26

The structure of quartz (empirical formula SiO_2). Quartz contains chains of SiO_4 tetrahedra that share oxygen atoms.

The bonding in the CO_2 molecule was described in Section 9.1.

abilities of carbon and silicon to form π bonds with oxygen have profound effects on the structures and properties of CO_2 and SiO_2.

Compounds closely related to silica and found in most rocks, soils, and clays are the **silicates.** Like silica, the silicates are based on interconnected SiO_4 tetrahedra. However, in contrast to silica, where the O:Si ratio is 2:1, silicates have O:Si ratios greater than 2:1 and contain silicon-oxygen *anions*. This means that to form the neutral solid silicates, cations are needed to balance the excess negative charge. In other words, silicates are salts containing metal cations and polyatomic silicon-oxygen anions. Examples of important silicate anions are shown in Fig. 10.27.

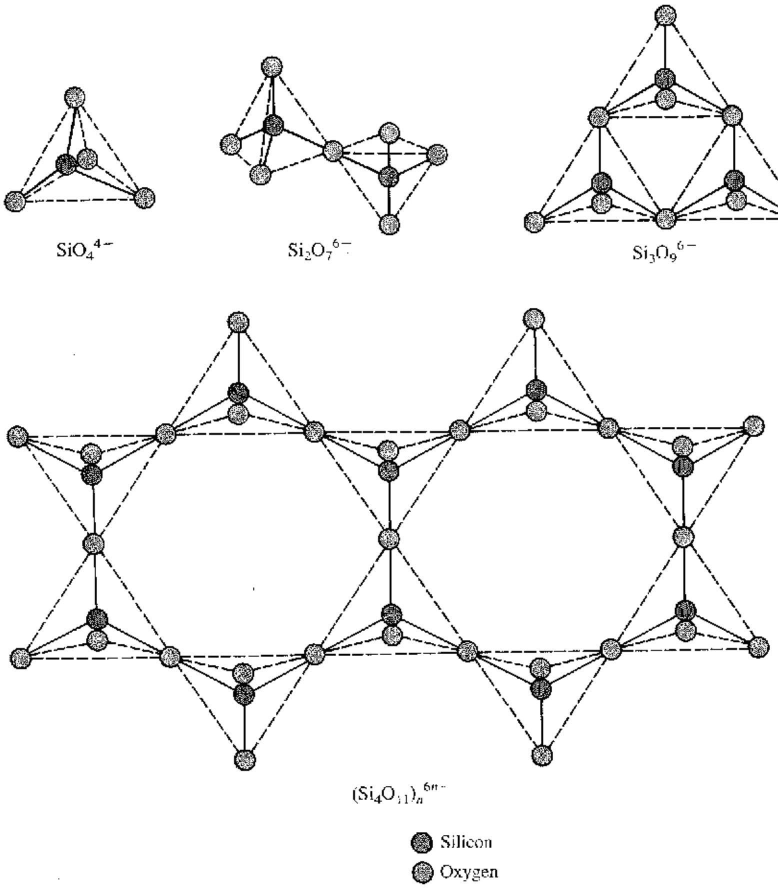


Figure 10.27

Examples of silicate anions, all of which are based on SiO_4^{4-} tetrahedron.

When silica is heated above its melting point (about 1600°C) and cooled rapidly, an amorphous solid called a **glass** results (see Fig. 10.28). Note that a glass contains a good deal of disorder, in contrast to the crystalline nature of quartz. Glass more closely resembles a very viscous solution than it does a crystalline solid. Common glass results when substances such as Na_2CO_3 are added to the silica melt, which is then cooled. The properties of glass can be varied greatly by varying the additives. For example, addition of B_2O_3 produces a glass (called borosilicate glass) that expands and contracts little under large temperature changes. Thus it is useful for labware and cooking utensils. The most common brand name for this glass is Pyrex. The addition of K_2O produces an especially hard glass that can be ground to the precise shapes needed for eyeglass and contact lenses. The compositions of several types of glass are shown in Table 10.4.

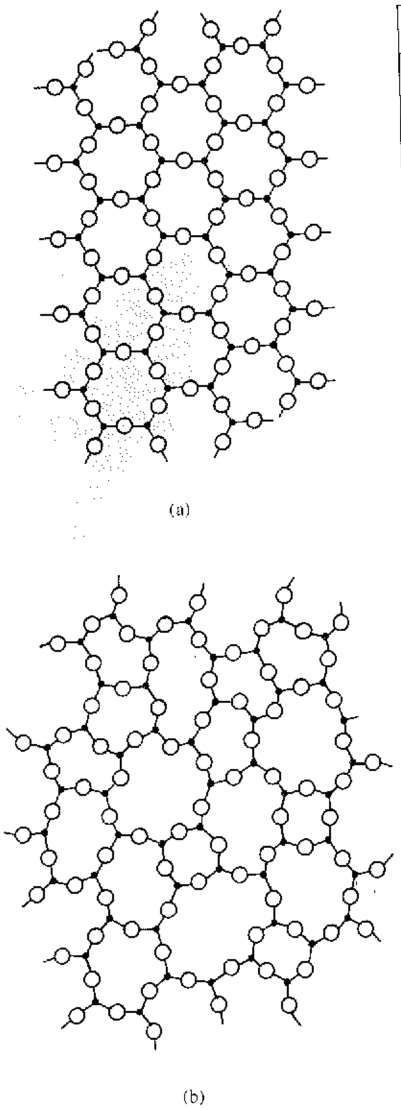


Figure 10.28

Two-dimensional representations of (a) a quartz crystal and (b) a quartz glass.

Compositions of Some Common Types of Glass

Type of glass	Percentages of various components						
	SiO_2	CaO	Na_2O	B_2O_3	Al_2O_3	K_2O	MgO
Window (soda-lime glass)	72	11	13	--	0.3	3.8	—
Cookware (aluminosilicate glass)	55	15	0	—	20	—	10
Heat-resistant (borosilicate glass)	76	3	5	13	2	0.5	--
Optical	69	12	6	0.3	—	12	—

Table 10.4

Ceramics

Ceramics are typically made from clays (which contain silicates) and hardened by firing at high temperatures. Ceramics are a class of nonmetallic materials that are strong, brittle, and resistant to heat and attack by chemicals.

Like glass, ceramics are based on silicates, but with that the resemblance ends. Glass can be melted and remelted as often as desired, but once a ceramic has been hardened, it is resistant to extremely high temperatures. This behavior results from the very different structures of glasses and ceramics. A glass is a *homogeneous*, noncrystalline "frozen solution," and a ceramic is *heterogeneous*. A ceramic contains two phases: minute crystals of silicates are suspended in a glassy cement.

To understand how ceramics harden, it is necessary to know something about the structure of clays. Clays are formed by the weathering action of water and carbon dioxide on the mineral feldspar, which is a mixture of silicates with empirical formulas such as $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ and $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$. Feldspar is really an **aluminosilicate** in which aluminum as well as silicon atoms are part of the oxygen-bridged polyanion. The weathering of feldspar produces kaolinite, consisting of tiny thin platelets with the empirical formula $Al_2SiO_5(OH)_4$. When dry, the platelets cling together; when water is present, they can slide over one another, giving clay its plasticity. As clay dries, the platelets begin to interlock again. When the remaining water is driven off during firing, the silicates and cations form a glass that binds the tiny crystals of kaolinite.

Ceramics have a very long history. Rocks, which are natural ceramic materials, served as the earliest tools. Later, clay vessels dried in the sun or baked in fires served as containers for food and water. These early vessels were no doubt crude and quite porous. With the discovery of glazing, which probably occurred about 3000 B.C. in Egypt, pottery became more serviceable as well as more beautiful. Prized porcelain is essentially the same material as crude earthenware, but specially selected clays and glazings are used for porcelain and the clay object is fired at a very high temperature.

Semiconductors

Elemental silicon has the same structure as diamond, as might be expected from its position in the periodic table (in Group 4A directly under carbon). Recall that in diamond there is a large energy gap between the filled and empty molecular orbitals (Fig. 10.26). This gap prevents excitation of electrons to the empty molecular

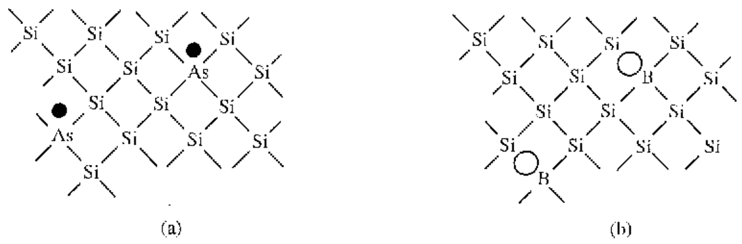


Figure 10.29

Semiconductors can be formed by doping silicon crystals. (a) A silicon crystal doped with arsenic, which has one extra valence electron. This is called an n-type semiconductor. (b) A silicon crystal doped with boron, which has one less electron than silicon. This is called a p-type semiconductor.

orbitals (conduction bands) and makes diamond an insulator. In silicon the situation is similar but the energy gap is smaller. A few electrons can cross the gap at 25°C, making silicon a *semiconducting element,* or **semiconductor.** In addition, at higher temperatures, where more energy is available to excite electrons into the conduction bands, the conductivity of silicon increases. This is typical behavior for a semiconducting element and is in contrast to that of metals, whose conductivity decreases with increasing temperature.

The small conductivity of silicon can be enhanced at normal temperatures if the silicon crystal is *doped* with certain other elements. For example, when a small fraction of silicon atoms is replaced by arsenic atoms, each having *one more* valence electron than silicon, extra electrons become available for conduction, as shown in Fig. 10.29(a). This produces an **n-type semiconductor,** a substance whose conductivity is increased by doping it with atoms having more valence electrons than the atoms in the host crystal. These extra electrons lie close in energy to the conduction bands and can easily be excited into these levels, where they can conduct an electric current [see Fig. 10.30(a)].

The name n-type follows from the negative charge carriers (the electrons).

We can also enhance the conductivity of silicon by doping the crystal with an element such as boron, which has only three valence electrons, one *less* than silicon. Because boron has one less electron than is required to form the bonds to the surrounding silicon atoms, an electron vacancy, or *hole,* is created, as shown in Fig. 10.29(b). As an electron fills this hole, it leaves a new hole, and this process can be repeated. Thus the hole advances through the crystal in a direction opposite to movement of the electrons jumping to fill the hole. Another way of thinking about this phenomenon is that in pure silicon each atom has four valence electrons, and the low-energy molecular orbitals are exactly filled. Replacing silicon atoms with boron atoms leaves vacancies in these molecular orbitals, as shown in Fig. 10.30(b). This means there is only one electron in some of the molecular orbitals,

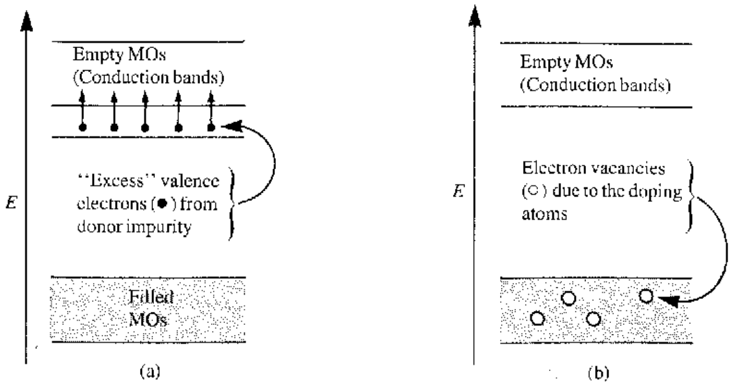


Figure 10.30

Energy-level diagrams for (a) an n-type semiconductor and (b) a p-type semiconductor. In the n-type semiconductor, atoms with more valence electrons than the atoms in the host crystal are inserted. These extra electrons lie close in energy to the empty molecular orbitals and can easily be excited into these levels. (b) In the p-type semiconductor, atoms with fewer valence electrons than the atoms of the host crystal are inserted. As a result, some molecular orbitals contain only one electron, and these unpaired electrons can act as conductors.

Electrons must be in singly occupied molecular orbitals to conduct a current.

and these unpaired electrons can function as conducting electrons. Thus the substance becomes a better conductor. When semiconductors are doped with atoms having fewer valence electrons than the atoms of the host crystal, they are called **p-type semiconductors,** so named because the positive holes can be viewed as the charge carriers.

Most important applications of semiconductors involve connection of a p-type and an n-type to form a **p-n junction.** Figure 10.31(a) shows a typical junction; the dark circles represent excess electrons in the n-type semiconductor, and the white circles represent holes (electron vacancies) in the p-type semiconductor. At the junction a small number of electrons migrate from the n-type region into the p-type region, where there are vacancies in the low-energy molecular orbitals. The effect of these migrations is to place a negative charge on the p-type region (since it now has a surplus of electrons) and a positive charge on the n-type region (since it has lost electrons, leaving holes in its low-energy molecular orbitals). This charge build-up, called the *contact potential,* or *junction potential,* prevents further migration of electrons.

Now suppose an external electrical potential is applied by connecting the negative terminal of a battery to the p-type region and the positive terminal to the n-type region. The situation represented in Fig. 10.31(b) results. Electrons are drawn toward the positive terminal, and the resulting holes move toward the negative terminal—exactly opposite to the natural flow of electrons at the p-n junction. The junction resists the imposed current flow in this direction and is said to be under *reverse bias.* No current flows through the system.

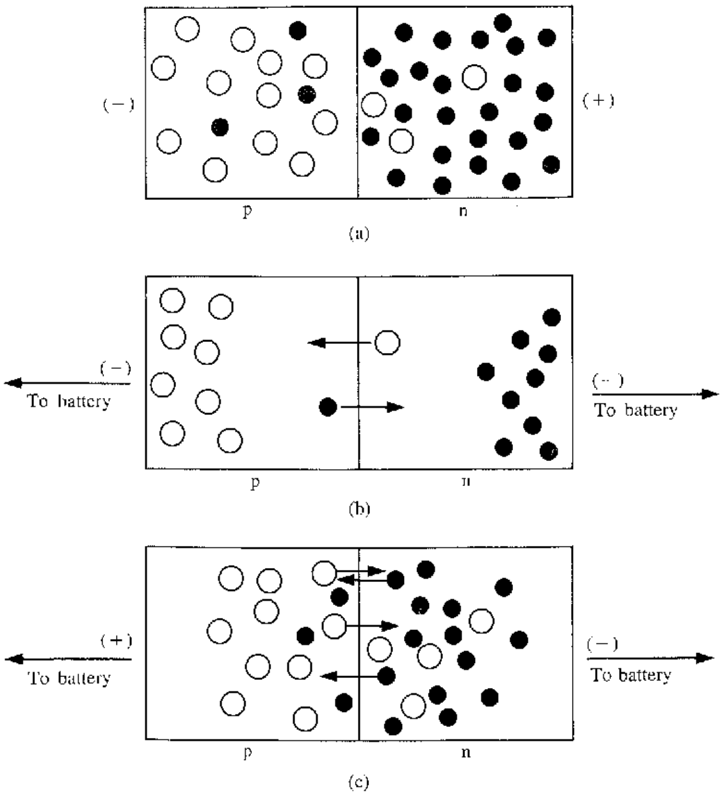


Figure 10.31

The p-n junction involves the contact of a p-type and an n-type semiconductor. (a) The charge carriers of the p-type region are holes (○). In the n-type region the charge carriers are electrons (•). On contact there is a natural migration of some electrons from the n-type region to the p-type region, setting up a junction potential where the p-type region is negative and the n-type region is positive. (b) An applied external potential, where the p-type region is connected to the negative terminal of the battery and the n-type region is connected to the positive terminal, tries to force the charge carriers to flow in the direction opposite to the natural flow. No current flows (reverse bias). (c) When a p-n junction is attached to a battery with the p-type region connected to the positive terminal and the n-type region to the negative terminal, current readily flows (forward bias). Note that each electron that crosses the boundary leaves a hole behind. Thus the electrons and the holes move in opposite directions.

On the other hand, if the battery is connected so that the negative terminal is connected to the n-type region and the positive terminal is connected to the p-type region [Fig. 10.31(c)], the movement of electrons (and holes) is in the favored direction. The junction has low resistance, and a current flows easily. The junction is said to be under *forward bias*.

A p-n junction makes an excellent *rectifier*, a device that produces direct current (flows in one direction) from an alternating current (flows in both directions alternately). When placed in a circuit where the potential is constantly reversing, a p-n junction transmits current only under forward bias, thus converting the alternating current to a direct current. Radios, computers, and other electrical devices formerly used bulky, unreliable vacuum tubes as rectifiers. The p-n junction has revolutionized electronics; modern solid-state components contain p-n junctions in printed circuits.

Printed circuits are discussed in the Chemical Impact feature at the end of this chapter.

10.6 Molecular Solids

PURPOSE

☐ To describe the bonding in molecular solids.

So far we have considered solids in which atoms occupy the lattice positions, and in most cases such a crystal can be considered to be one giant molecule. However, there are many types of solids that contain discrete molecular units at each lattice position. The most common example is ice, where the lattice positions are occupied by water molecules [see Fig. 10.12(c)]. Other examples are dry ice (solid carbon dioxide), some forms of sulfur that contain S_8 molecules [Fig. 10.32(a)],

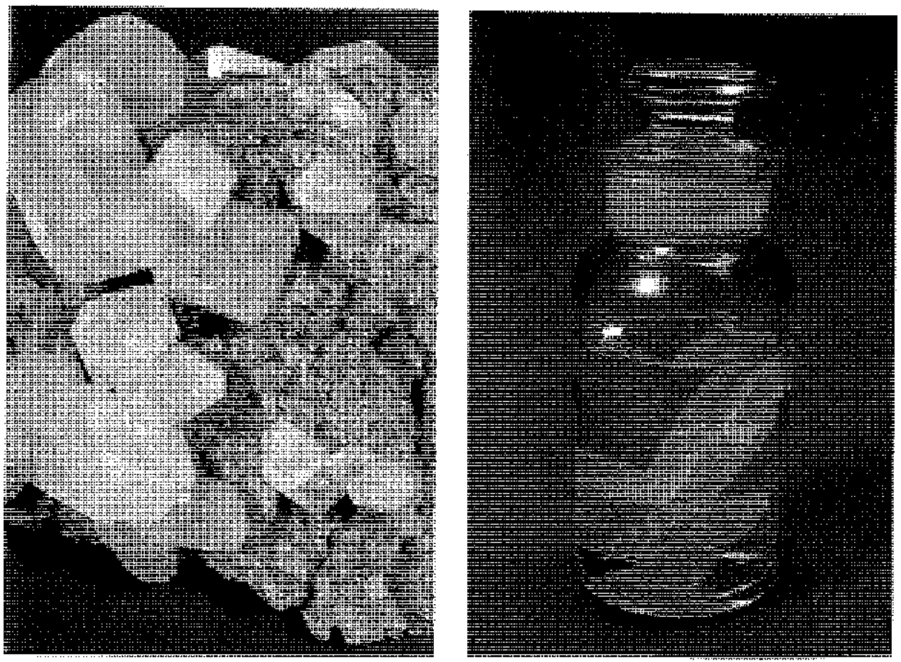


Figure 10.32

(a) Sulfur crystals contain S_8 molecules. (b) White phosphorus contains P_4 molecules. It is so reactive with the oxygen in air that it must be stored under water.

and certain forms of phosphorus that contain P_4 molecules [Fig. 10.32(b)]. These substances are characterized by strong covalent bonding *within* the molecules but relatively weak forces *between* the molecules. For example, it takes only 6 kJ of energy to melt 1 mole of solid water (ice) because only intermolecular ($H_2O—H_2O$) interactions must be overcome. However, 470 kJ of energy is required to break a mole of covalent O—H bonds. The differences between the covalent bonds within the molecules and the forces between the molecules are apparent from the comparison of the interatomic and intermolecular distances in Table 10.5.

Comparison of Atomic Separations Within Molecules (Covalent Bonds) and Between Molecules (Intermolecular Interactions).

Solid	Distance between atoms in molecule*	Closest distance between molecules
P_4	2.20 Å	3.8 Å
S_8	2.06 Å	3.7 Å
Cl_2	1.99 Å	3.6 Å

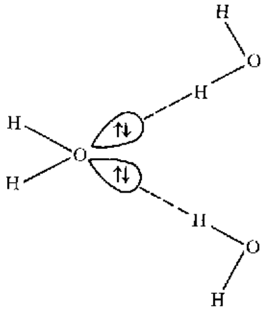
---

*The shorter distances within the molecules indicate stronger bonding.

Table 10.5

The forces that exist among the molecules in a molecular solid depend on the nature of the molecules. Many molecules such as CO_2, I_2, P_4, and S_8 have no dipole moment, and the intermolecular forces are the relatively weak London dispersion forces. Because these forces are usually small, we might expect all of these substances to be gaseous at 25°C, as is the case for carbon dioxide. However, as the size of the molecules increases, the London forces become larger, causing many of these substances to be solids at 25°C.

When molecules do have dipole moments, their intermolecular forces are significantly greater, especially when hydrogen bonding is possible. Water molecules are particularly well suited to interact with each other because each molecule has two polar O—H bonds and two lone pairs on the oxygen atom. This can lead to the association of four hydrogen atoms with each oxygen: two by covalent bonds and two by dipole forces.



Note the two relatively short covalent oxygen-hydrogen bonds and the two longer oxygen-hydrogen dipole interactions that can be seen in the ice structure in Fig. 10.12(c).

10.7 | Ionic Solids

PURPOSE

- To model the structures of ionic solids using the packing of spheres.

Ionic solids are stable, high-melting substances held together by the strong electrostatic forces that exist between oppositely charged ions. The principles governing the structures of ionic solids were introduced in Section 8.5. In this section we will review and extend these principles.

The structures of most binary ionic solids, such as sodium chloride, can be explained by the closest packing of spheres. Typically, the larger ions, usually the anions, are packed in one of the closest packing arrangements (hcp or ccp), and the smaller cations fit into holes among the close packed anions. The packing is done in a way that maximizes the electrostatic attractions among oppositely charged ions and minimizes the repulsions among identically charged ions.

There are three types of holes in closest packed structures:

1. Trigonal holes are formed by three spheres in the same layer [Fig. 10.33(a)].
2. Tetrahedral holes are formed when a sphere sits in the dimple of three spheres in an adjacent layer [Fig. 10.33(b)].
3. Octahedral holes are formed between two sets of three spheres in adjoining layers of the closest packed structures [Fig. 10.33(c)].

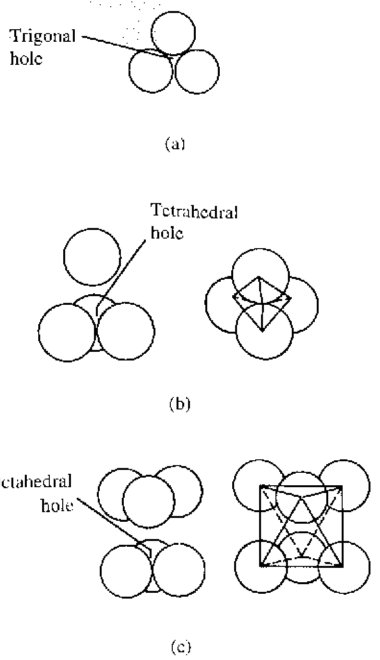


Figure 10.33

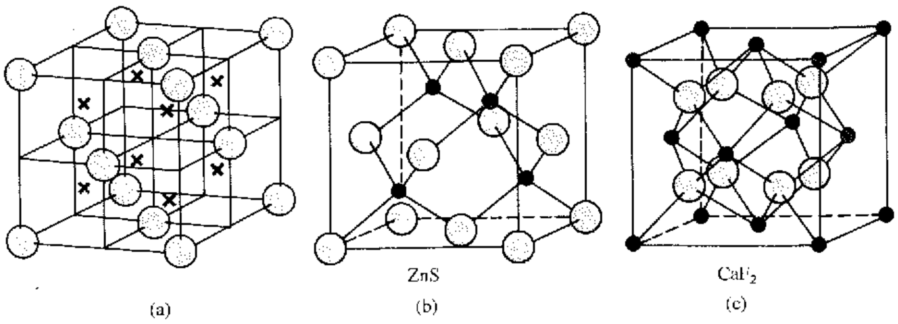
The holes that exist among closest packed uniform spheres. (a) The trigonal hole formed by three spheres in a given plane. (b) The tetrahedral hole formed when a sphere occupies a dimple in an adjacent layer. (c) The octahedral hole formed by six spheres in two adjacent layers.

For spheres of a given diameter, the holes increase in size in the order:

Trigonal < tetrahedral < octahedral

In fact, trigonal holes are so small that they are never occupied in binary ionic compounds. Whether the tetrahedral or octahedral holes in a given binary ionic solid are occupied depends mainly on the *relative* sizes of the anion and cation. For example, in zinc sulfide the S^{2-} ions (ionic radius = 1.8 Å) are arranged in a cubic closest packed structure with the smaller Zn^{2+} ions (ionic radius = 0.7 Å) in the tetrahedral holes. The location of the tetrahedral holes in the face-centered cubic unit cell of the ccp structure is shown in Fig. 10.34(a). Note from this figure that there are eight tetrahedral holes in the unit cell. Also recall from the discussion in Section 10.4 that there are four net spheres in the face-centered cubic unit cell. Thus there are *twice as many tetrahedral holes as packed anions* in the closest packed structure. Zinc sulfide must have the same number of S^{2-} ions and Zn^{2+} ions to achieve electrical neutrality. Thus in the zinc sulfide structure only *half* of the tetrahedral holes contain Zn^{2+} ions, as shown in Fig. 10.34(b).

In the closest packed structures, there are twice as many tetrahedral holes as packed spheres.



(a) (b) (c)

Figure 10.34

(a) The locations (x) of the eight tetrahedral holes in the face-centered cubic unit cell. (b) The unit cell for ZnS where the S^{2-} ions (○) are closest packed with the Zn^{2+} ions (●) in alternate tetrahedral holes. (c) The unit cell for CaF_2 where the Ca^{2+} ions (●) are closest packed with the F^- ions (○) in all of the tetrahedral holes.

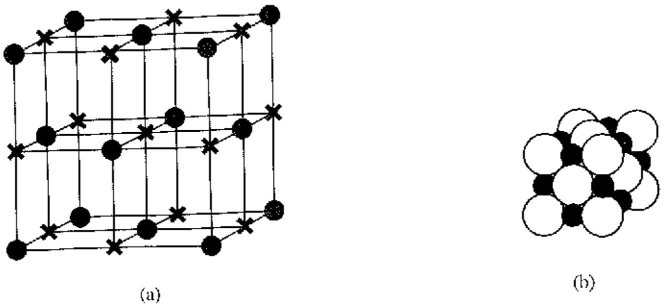

(a) (b)

Figure 10.35

(a) The locations (x) of the octahedral holes in the face-centered cubic unit cell. (b) Representation of the unit cell for solid NaCl. The Cl^- ions have a ccp arrangement with Na^+ ions in all of the octahedral holes.

The structure of calcium fluoride (CaF_2) can be similarly explained. However, in this case the structure is best visualized as a cubic closest packed array of Ca^{2+} ions with F^- ions in *all* of the tetrahedral holes [Fig. 10.34(c)]. This produces the required 2:1 stoichiometry.

The structure of sodium chloride can be described in terms of a cubic closest packed array of Cl^- ions with Na^+ ions in all of the octahedral holes. The location of the octahedral holes in the face-centered cubic unit cell is shown in Fig. 10.35(a). The easiest octahedral hole to find in this structure is the one at the center of the cube. Note that this hole is surrounded by six spheres, as is required to form an octahedron. The remaining octahedral holes are shared with other unit cells and are more difficult to visualize. However, it can be shown that the number of octahedral holes in the ccp structure is the *same* as the number of packed anions. Figure 10.35(b) shows the structure for sodium chloride that results from Na^+ ions filling all of the octahedral holes in a ccp array of Cl^- ions.

In the closest packed structures, there are the same number of octahedral holes as packed spheres.

A great variety of ionic solids exists. Our purpose in this section is not to give an exhaustive treatment of ionic solids, but to emphasize the fundamental principles governing their structures. As we have seen, the most useful model for explaining the structures of these solids regards the ions as hard spheres that are packed to maximize attractions and minimize repulsions.

Sample Exercise 10.4

Determine the net number of Na^+ and Cl^- ions in the sodium chloride unit cell.

Solution

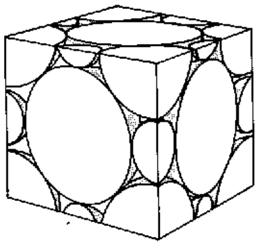
Note from Fig. 10.35(b) that the Cl^- ions are cubic closest packed and thus form a face-centered cubic unit cell. There is a Cl^- ion on each corner and one at the center of each face of the cube. Thus the net number of Cl^- ions present in a unit cell is

$$8(\tfrac{1}{8}) + 6(\tfrac{1}{2}) = 4$$

The Na^+ ions occupy the octahedral holes located in the center of the cube and midway along each edge. The Na^+ ion in the center of the cube is contained entirely in the unit cell, while those on the edges are shared by four unit cells (four cubes share a common edge). Since the number of edges in a cube is 12, the net number of Na^+ ions present is

$$1(1) + 12(\tfrac{1}{4}) = 4$$

We have shown that the net number of ions in a unit cell is 4 Na^+ ions and 4 Cl^- ions, which agrees with the 1:1 stoichiometry of sodium chloride.



In this chapter we have considered various types of solids. Table 10.6 summarizes these types of solids and some of their properties.

Types and Properties of Solids

	Type of Solid			
	Molecular	Atomic		Ionic
		Network	Metallic	
Structural unit	Molecule	Atom	Atom	Ion
Type of bonding	Polar molecules: dipole-dipole interactions Nonpolar molecules: London dispersion forces	Highly directional covalent bonds	Nondirectional covalent bonds involving electrons that are delocalized throughout the crystal	Electrostatic
Typical properties	Soft	Hard	Wide range of hardness	Hard
	Low melting point	High melting point	Wide range of melting points	High melting point
	Insulator	Insulator	Conductor	Insulator
Examples	Ice (solid H_2O) Dry ice (solid CO_2)	Diamond Graphite* Silicon†	Silver Iron Brass	Sodium chloride Calcium fluoride

*A conductor
†A semiconductor

Table 10.6

Sample Exercise 10.5

Using Table 10.6, classify each of the following substances according to the type of solid it forms:

a. gold
b. carbon dioxide
c. lithium fluoride
d. krypton

Solution

a. Solid gold is an atomic solid with metallic properties.
b. Solid carbon dioxide contains nonpolar carbon dioxide molecules and is a molecular solid.
c. Solid lithium fluoride contains Li^+ and F^- ions and is a binary ionic solid.
d. Solid krypton contains krypton atoms that can interact only through London dispersion forces. It is an atomic solid but has properties characteristic of a molecular solid with nonpolar molecules.

10.8 Vapor Pressure and Changes of State

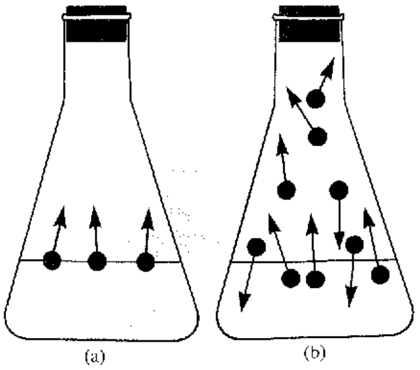


Figure 10.36

Behavior of a liquid in a closed container. (a) Initially net evaporation occurs as molecules are transferred from the liquid to the vapor phase, so the amount of liquid decreases. (b) As the number of vapor molecules increases, the rate of return to the liquid (condensation) increases, until finally the rate of condensation equals the rate of evaporation. The system is at equilibrium, and no further changes occur in the amounts of vapor or liquid.

PURPOSE

- To define the vapor pressure of a liquid.
- To discuss the features of heating curves.

Now that we have considered the general properties of the three states of matter, we can explore the processes by which matter changes state. One very familiar example of a change in state occurs when a liquid evaporates from an open container. This is clear evidence that the molecules of a liquid can escape the liquid's surface and form a gas. Called **vaporization,** or *evaporation,* this process is endothermic because energy is required to overcome the relatively strong intermolecular forces in the liquid. The energy required to vaporize 1 mole of a liquid at a pressure of 1 atm is called the **heat of vaporization,** or the enthalpy of vaporization, and is usually symbolized as ΔH_{vap}.

The endothermic nature of vaporization has great practical significance; in fact, one of the most important roles that water plays in our world is to act as a coolant. Because of the strong hydrogen bonding among its molecules in the liquid state, water has an unusually large heat of vaporization (41.2 kJ/mol). A significant portion of the sun's energy that reaches earth is spent evaporating water from the oceans, lakes, and rivers rather than warming the earth. The vaporization of water is also crucial to the body's temperature control system through evaporation of perspiration.

Vapor Pressure

When a liquid is placed in a closed container, the amount of liquid at first decreases but eventually becomes constant. The decrease occurs because there is an initial net transfer of molecules from the liquid to the vapor phase (Fig. 10.36). However, as the number of vapor molecules increases, so does the rate of return of these molecules to the liquid. The process by which vapor molecules reform a liquid is called **condensation.** Eventually enough vapor molecules are present above the liquid so that the rate of condensation equals the rate of evaporation (see Fig. 10.37). *At this point no further net change occurs in the amount of liquid or vapor because the two*

Vapor is the usual term for the gas phase of a substance that exists as a solid or liquid at 25°C and 1 atm.

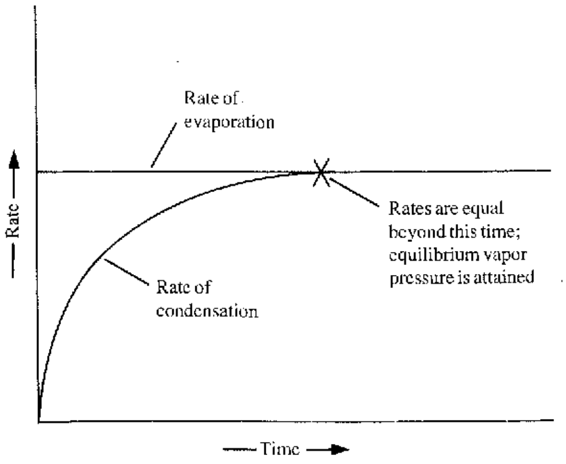


Figure 10.37

The rates of condensation and evaporation over time for a liquid sealed in a closed container. The rate of evaporation remains constant and the rate of condensation increases as the number of molecules in the vapor phase increases, until the two rates become equal. At this point, the equilibrium vapor pressure is attained.

opposite processes exactly balance each other; the system is at **equilibrium.** Note that this system is highly *dynamic* on the molecular level—molecules are constantly escaping from and entering the liquid at a high rate. However, there is no *net* change because the two opposite processes just *balance* each other.

A system at equilibrium is dynamic on the molecular level, but shows no macroscopic changes.

The pressure of the vapor present at equilibrium is called the *equilibrium vapor pressure,* or more commonly, the **vapor pressure** of the liquid. A simple barometer can measure the vapor pressure of a liquid, as shown below in Fig. 10.38(a). The liquid is injected at the bottom of the tube of mercury and floats to the surface because the mercury is so dense. The liquid evaporates at the top of the column, producing a vapor whose pressure pushes some mercury out of the tube. When the system reaches equilibrium, the vapor pressure can be determined from the change in the height of the mercury column since

$$P_{\text{atmosphere}} = P_{\text{vapor}} + P_{\text{Hg column}}$$

Thus

$$P_{\text{vapor}} = P_{\text{atmosphere}} - P_{\text{Hg column}}$$

The vapor pressures of liquids vary widely [see Fig. 10.38(b)]. Liquids with high vapor pressures are said to be *volatile*—they evaporate rapidly from an open dish.

The vapor pressure of a liquid is affected by two main factors: the *molecular weight* and the *intermolecular forces.* Molecular weight is important because at a given temperature heavy molecules have lower velocities than light molecules and thus have a much smaller tendency to escape from the liquid surface. A liquid with a high molecular weight tends to have a small vapor pressure. Liquids in which the intermolecular forces are large also have relatively low vapor pressures because the molecules need high energies to escape to the vapor phase. For example, although water has a much lower molecular weight than that of diethyl ether, the strong hydrogen bonding forces that exist among water molecules in the liquid cause water's vapor pressure to be much lower than that of diethyl ether [see Fig. 10.38(b)].

Heavy molecules have lower velocities than light ones at a given temperature.

Measurements of the vapor pressure for a given liquid at several temperatures show that *vapor pressure increases significantly with temperature.* Figure 10.39 on the following page shows the distribution of molecular velocities in a liquid at two temperatures. To overcome the intermolecular forces in a liquid, a molecule must

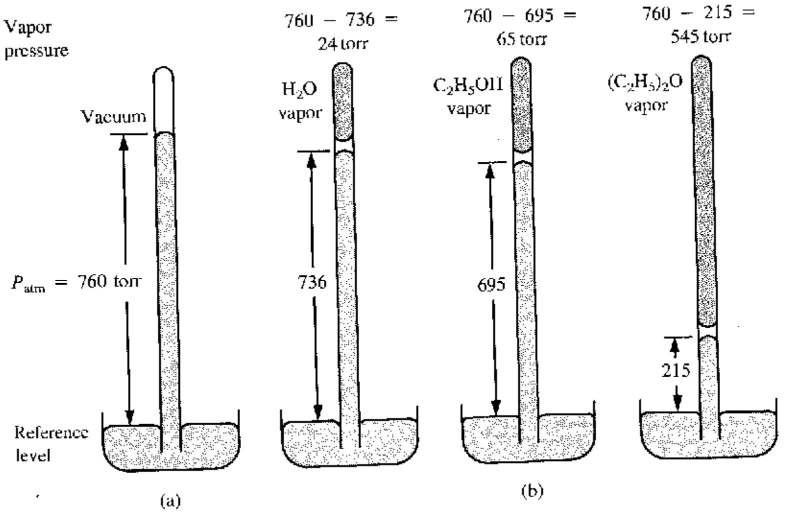
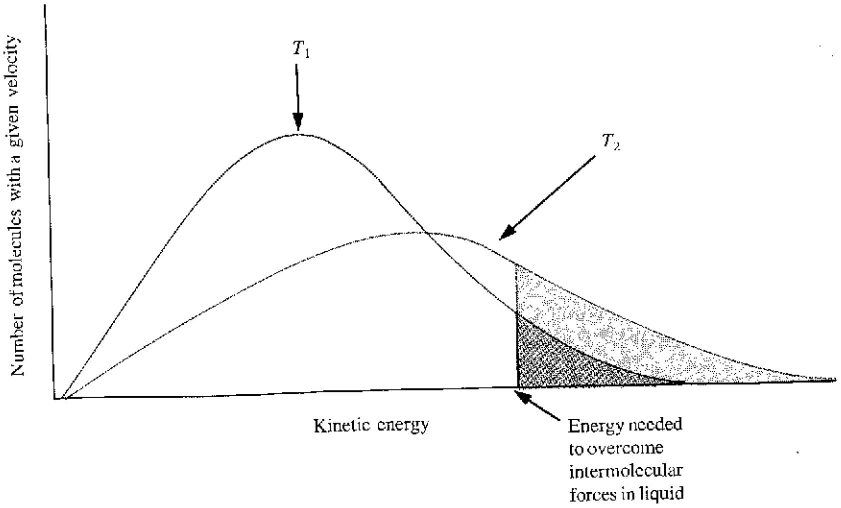


Figure 10.38

(a) The vapor pressure of a liquid can be easily measured using a simple barometer of the type shown here. (b) The three liquids water, ethanol (C_2H_5OH), and diethyl ether [$(C_2H_5)_2O$] have quite different vapor pressures. Ether is by far the most volatile of the three.

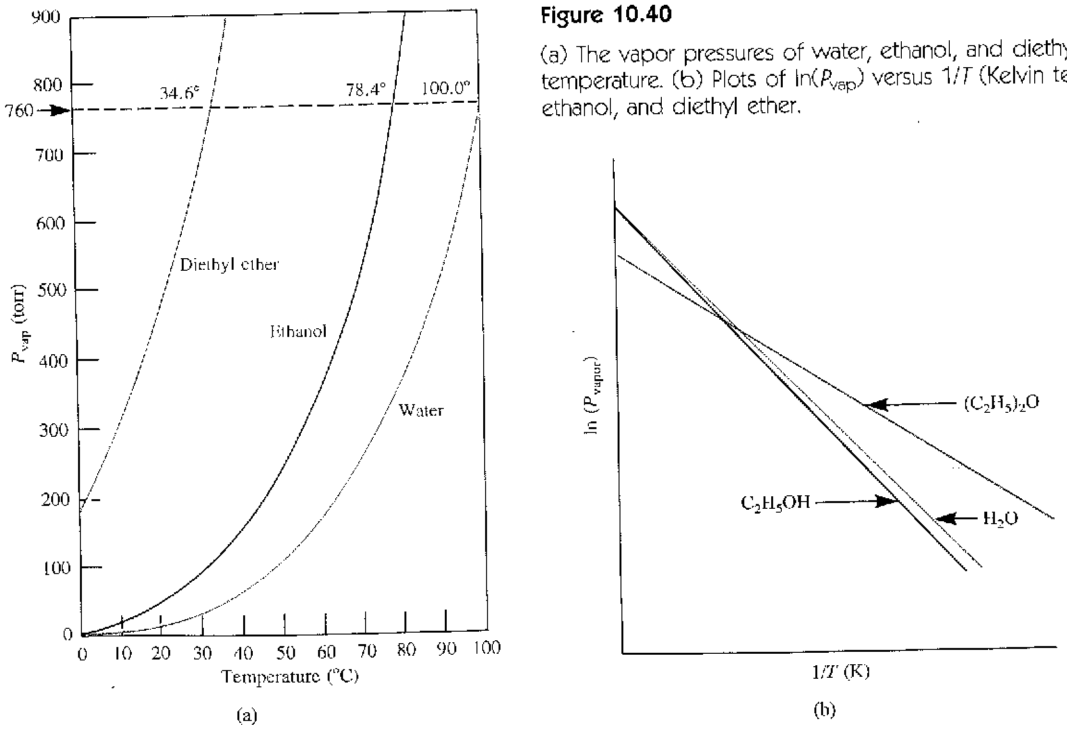
Figure 10.39

The number of molecules in a liquid with a given kinetic energy versus kinetic energy at two temperatures, where $T_2 > T_1$. The energy necessary for molecules to overcome the intermolecular forces in the liquid and to escape to the vapor phase is indicated. Note that the proportion of molecules with enough energy to escape (indicated by shaded areas) increases dramatically with temperature. This causes vapor pressure to increase markedly with temperature.



have a minimum kinetic energy. As the temperature of the liquid is increased, the fraction of molecules having sufficient energy to overcome these forces and escape to the vapor phase increases markedly. Thus the vapor pressure of a liquid increases dramatically with temperature.

The quantitative nature of the temperature dependence of vapor pressure can be determined graphically. Plots of vapor pressure versus temperature for water, ethanol, and diethyl ether are shown in Fig. 10.40(a). Note the nonlinear increase in



(a)

(b)

Figure 10.40

(a) The vapor pressures of water, ethanol, and diethyl ether as a function of temperature. (b) Plots of ln(P_{vap}) versus 1/T (Kelvin temperature) for water, ethanol, and diethyl ether.

vapor pressure for all the liquids as the temperature is increased. We find that a straight line can be obtained by plotting $\ln(P_{\text{vap}})$ versus $1/T$, where T is the Kelvin temperature, as shown in Fig. 10.40(b). We can represent this behavior by the equation

$$\ln(P_{\text{vap}}) = -\frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T}\right) + C \qquad (10.4)$$

where ΔH_{vap} is the heat of vaporization, R is the universal gas constant, and C is a constant characteristic of a given liquid. The symbol ln means that the natural logarithm of the vapor pressure should be taken.

Natural logarithms are reviewed in Appendix 1.2.

Equation (10.4) is the equation of a straight line of the form $y = mx + b$, where

$$y = \ln(P_{\text{vap}})$$

$$x = \frac{1}{T}$$

$$m = \text{slope} = -\frac{\Delta H_{\text{vap}}}{R}$$

$$b = \text{intercept} = C$$

Sample Exercise 10.6

Using the plots in Fig. 10.40(b), determine whether water or diethyl ether has the larger heat of vaporization.

Solution

When $\ln(P_{\text{vap}})$ is plotted versus $1/T$, the slope of the resulting straight line is

$$-\frac{\Delta H_{\text{vap}}}{R}$$

Note from Fig. 10.40(b) that the slopes of the lines for water and diethyl ether are both negative, as expected, and that the line for ether has the smaller slope. Thus ether has the smaller value of ΔH_{vap}. This makes sense because the hydrogen bonding in water causes it to have a relatively large heat of vaporization.

Equation (10.4) is important for several reasons. For example, we can determine the heat of vaporization for a liquid by measuring P_{vap} at several temperatures and then evaluating the slope of a plot of $\ln(P_{\text{vap}})$ versus $1/T$. On the other hand, if we know the value of ΔH_{vap} and P_{vap} at one temperature, we can use Equation (10.4) to calculate P_{vap} at another temperature. This can be done by recognizing that the constant C does not depend on temperature. Thus at two temperatures, T_1 and T_2, we can solve Equation (10.4) for C and then write the equality

$$\ln(P_{\text{vap}}^{T_1}) + \frac{\Delta H_{\text{vap}}}{RT_1} = C = \ln(P_{\text{vap}}^{T_2}) + \frac{\Delta H_{\text{vap}}}{RT_2}$$

This can be rearranged to

$$\ln(P_{\text{vap}}^{T_1}) - \ln(P_{\text{vap}}^{T_2}) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

or

$$\ln\left(\frac{P_{\text{vap}}^{T_1}}{P_{\text{vap}}^{T_2}}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{10.5}$$

Sample Exercise 10.7

The vapor pressure of water at 25°C is 23.8 torr, and the heat of vaporization of water is 41.2 kJ/mol. Calculate the vapor pressure of water at 50°C.

Solution

We will use Equation (10.5):

$$\ln\left(\frac{P_{\text{vap}}^{T_1}}{P_{\text{vap}}^{T_2}}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

For water we have

$$P_{\text{vap}}^{T_1} = 23.8 \text{ torr}$$
$$T_1 = 25 + 273 = 298 \text{ K}$$
$$T_2 = 50 + 273 = 323 \text{ K}$$
$$\Delta H_{\text{vap}} = 41.2 \text{ kJ/mol} = 41{,}200 \text{ J/mol}$$
$$R = 8.3148 \text{ J/K mol}$$

Thus

$$\ln\left(\frac{23.8 \text{ torr}}{P_{\text{vap}}^{T_2}\ (\text{torr})}\right) = \left(\frac{1}{323 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$

$$\ln\left(\frac{23.8}{P_{\text{vap}}^{T_2}}\right) = -1.288$$

Taking the antilog (see Appendix 1.2) of both sides gives

$$\frac{23.8}{P_{\text{vap}}^{T_2}} = 0.276$$

$$P_{\text{vap}}^{T_2} = 86.2 \text{ torr}$$

Like liquids, solids have vapor pressures. Figure 10.41 shows iodine vapor in equilibrium with solid iodine in a closed flask. Under normal conditions iodine *sublimes;* that is, it goes directly from the solid to the gaseous state without passing through the liquid state. **Sublimation** also occurs with dry ice (solid carbon dioxide).

Phase changes of carbon dioxide are discussed in Section 10.9.

Changes of State

What happens when a solid is heated? Typically, it will melt to form a liquid. If the heating continues, the liquid will at some point boil and form the vapor phase. This process can be represented by a **heating curve:** a plot of temperature versus time for a process where energy is added at a constant rate.

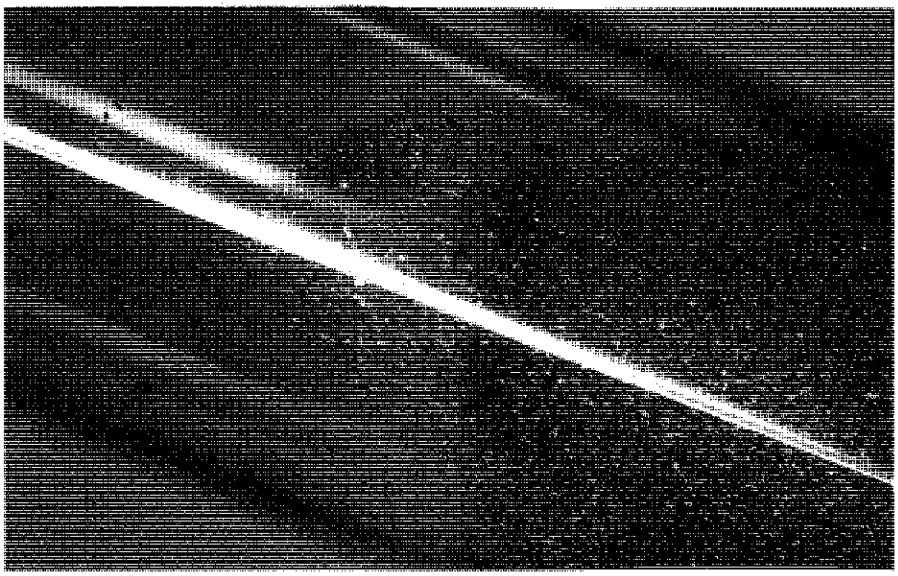


Figure 10.41

A closed flask containing solid iodine in equilibrium with its vapor [$I_2(g)$].

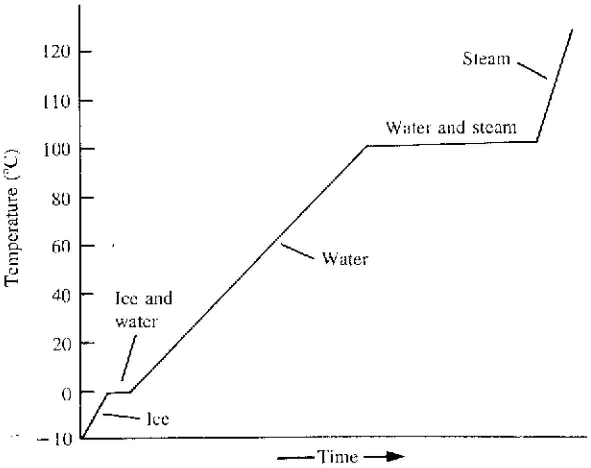


Figure 10.42

The heating curve for a given quantity of water where energy is added at a constant rate. The plateau at the boiling point is longer than the plateau at the melting point because it takes almost seven times more energy (and thus seven times the heating time) to vaporize liquid water than to melt ice. The slopes of the other lines are different because the different states of water have different heat capacities (the energy required to raise the temperature of 1 mole of a substance by 1°C).

The heating curve for water is given in Fig. 10.42. As energy flows into the ice, the random vibrations of the water molecules increase and the temperature rises. Eventually the molecules become so energetic that they break loose from their lattice positions, and the change from solid to liquid occurs. This is indicated by a plateau at 0°C on the heating curve. At this temperature, called the *melting point,* all of the added energy is used to disrupt the ice structure by breaking the hydrogen bonds, thus increasing the potential energy of the water molecules. The enthalpy change that occurs when a solid melts is called the **heat of fusion, ΔH_{fus}.**

The melting and boiling points will be defined more precisely later in this section.

The temperature remains constant until the solid has completely changed to liquid, then it begins to increase again. At 100°C the liquid water reaches its *boiling point,* and the temperature then remains constant as the added energy is used to vaporize the liquid. When the liquid is completely changed to vapor, the temperature again begins to rise. Note that changes of state are physical changes; although

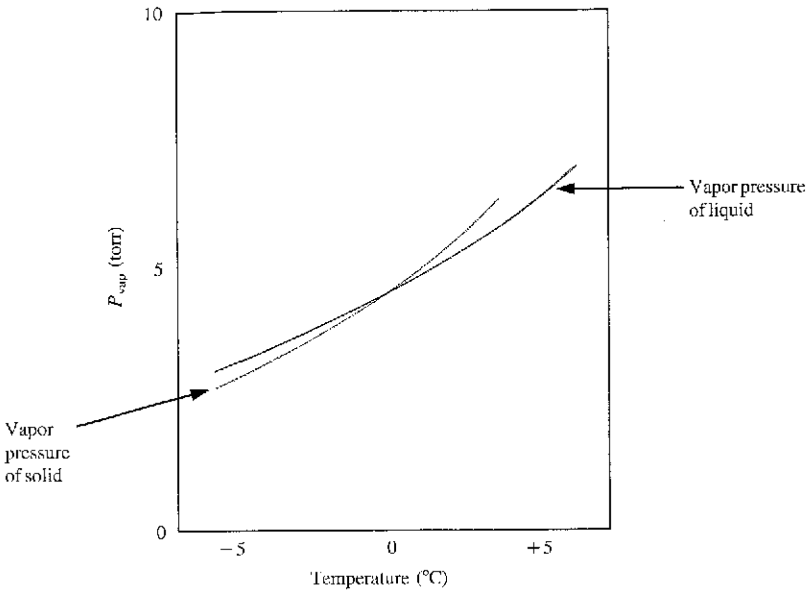


Figure 10.43

The vapor pressures of solid and liquid water as a function of temperature. The data for liquid water below 0°C are obtained from supercooled water. The data for solid water above 0°C are estimated by extrapolation of vapor pressure from below 0°C.

intermolecular forces have been overcome, no chemical bonds have been broken. If the water vapor were heated to much higher temperatures, the water molecules would break down into the individual atoms. This would be a chemical change since covalent bonds are broken. We no longer have water.

The melting and boiling points for a substance are determined by the vapor pressures of the solid and liquid states. Figure 10.43 shows the vapor pressures of solid and liquid water as functions of temperature near 0°C. Note that below 0°C the vapor pressure of ice is less than the vapor pressure of liquid water. Also note that the vapor pressure of ice has a larger temperature dependence than that of the liquid. That is, the vapor pressure of ice increases more rapidly for a given rise in temperature than does the vapor pressure of water. Thus, as the temperature of the solid is increased, a point is eventually reached where the *liquid and solid have identical vapor pressures*. This is the melting point.

These concepts can be demonstrated experimentally using the apparatus illustrated in Fig. 10.44, where ice occupies one compartment and liquid water the other. Consider the following cases.

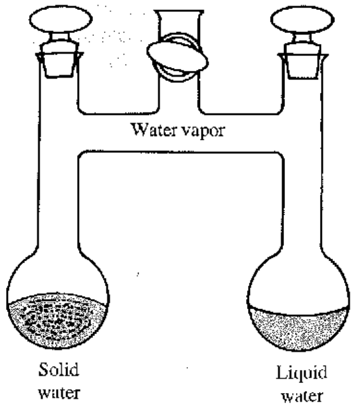


Figure 10.44

An apparatus that allows solid and liquid water to interact only through the vapor state.

Case 1. A temperature at which the vapor pressure of the solid is greater than that of the liquid. At this temperature the solid requires a higher pressure than the liquid does to be in equilibrium with the vapor. Thus, as vapor is released from the solid to try to achieve equilibrium, the liquid will absorb vapor in an attempt to reduce the vapor pressure to its equilibrium value. The net effect is a conversion from solid to liquid through the vapor phase. In fact, no solid can exist under these conditions. The amount of solid will steadily decrease and the volume of liquid will increase. Finally, there will be only liquid in the right compartment, which will come to equilibrium with the water vapor, and no further changes will occur in the system. This temperature must be *above the melting point* of ice, since only the liquid state can exist.

Case 2. A temperature at which the vapor pressure of the solid is less than that of the liquid. This is the opposite of the situation in Case 1. In this case, the liquid requires a higher pressure than the solid does to be in equilibrium with the vapor. So the liquid will gradually disappear, and the amount of ice will increase. Finally, only the solid will remain, which will achieve equilibrium with the vapor. This temperature must be *below the melting point* of ice, since only the solid state can exist.

Case 3. A temperature at which the vapor pressures of the solid and liquid are identical. In this case, the solid and liquid states have the same vapor pressure, so they can coexist in the apparatus at equilibrium simultaneously with the vapor. This temperature represents the *melting point* where both the solid and liquid states can exist.

We can now describe the melting point of a substance more precisely. The **normal melting point** is defined as *the temperature at which the solid and liquid states have the same vapor pressure under conditions where the total pressure is 1 atmosphere.*

Boiling occurs when the vapor pressure of a liquid becomes equal to the pressure of its environment. The **normal boiling point** of a liquid is *the temperature at which the vapor pressure of the liquid is exactly 1 atmosphere.* This concept is illustrated in Fig. 10.45. At temperatures where the vapor pressure of the liquid is less than 1 atmosphere, no bubbles of vapor can form because the pressure on the surface of the liquid is greater than the pressure in any spaces in the liquid where the bubbles are trying to form. Only when the liquid reaches a temperature at which the pressure of vapor in the spaces in the liquid is 1 atmosphere can bubbles form and boiling occur.

But changes of state do not always occur exactly at the boiling point or melting point. For example, water can be readily **supercooled;** that is, it can be cooled below 0°C at 1 atm pressure and remain in the liquid state. Supercooling occurs because, as it is cooled, the water may not achieve the degree of organization necessary to form ice at 0°C, and thus it continues to exist as the liquid. At some point the correct ordering occurs and ice rapidly forms, releasing energy in the exothermic process and bringing the temperature back up to the melting point, where the remainder of the water freezes (see Fig. 10.46 on the next page).

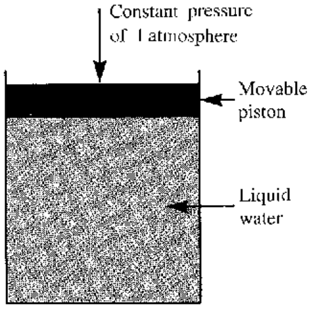


Figure 10.45

Water in a closed system with a pressure of 1 atm exerted on the piston. No bubbles can form within the liquid as long as the vapor pressure is less than 1 atm.

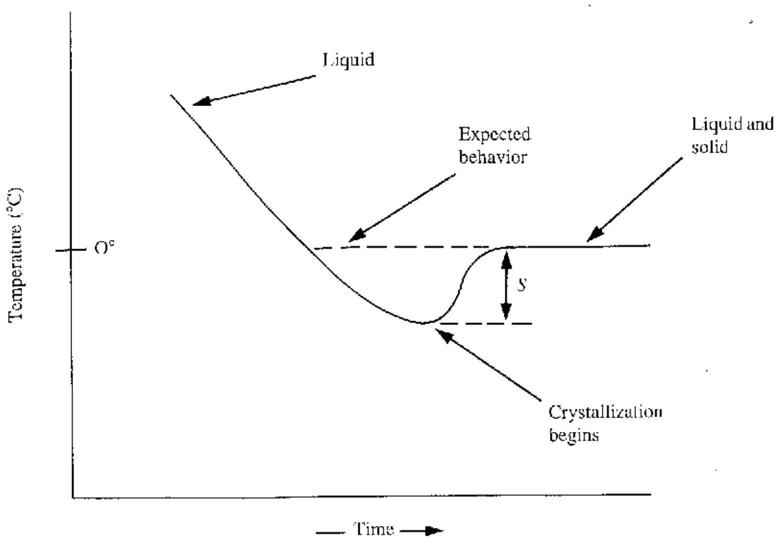


Figure 10.46

The supercooling of water. The extent of supercooling is given by S.

A liquid can also be **superheated,** or raised to temperatures above its boiling point, especially if it is heated rapidly. Superheating can occur because bubble formation in the interior of the liquid requires that many high-energy molecules gather in the same vicinity, and this may not happen at the boiling point, especially if the liquid is heated rapidly. If the liquid becomes superheated, the vapor pressure in the liquid is greater than the atmospheric pressure. Once a bubble does form, since its internal pressure is greater than that of the atmosphere, it can burst before rising to the surface, blowing the surrounding liquid out of the container. This is called *bumping,* and has ruined many experiments. It can be avoided by adding boiling chips to the flask containing the liquid. Boiling chips are bits of porous ceramic material containing trapped air that escapes on heating, forming tiny bubbles that act as ''starters'' for vapor bubble formation. This allows a smooth onset of boiling as the boiling point is reached.

10.9 Phase Diagrams

PURPOSE

- To discuss the features of phase diagrams.

A **phase diagram** is a convenient way of representing the phases of a substance as a function of temperature and pressure. For example, the phase diagram for water (Fig. 10.47) shows which state exists at a given temperature and pressure. It is important to recognize that a phase diagram describes conditions and events in a *closed* system of the type represented in Fig. 10.45, where no material can escape into the surroundings and no air is present.

To show how to interpret the phase diagram for water, we will consider heating experiments at several pressures, shown by the dashed lines in Fig. 10.48.

Experiment 1. Pressure is 1 atm. This experiment begins with the cylinder shown in Fig. 10.45 completely filled with ice at a temperature of −20°C, and

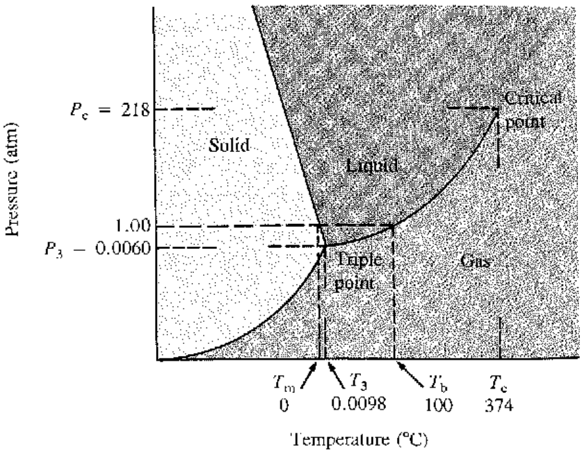


Figure 10.47

The phase diagram for water. T_m represents the normal melting point; T_3 and P_3 denote the triple point; T_b represents the normal boiling point; T_c represents the critical temperature; P_c represents the critical pressure. The negative slope of the solid/liquid line reflects the fact that the density of ice is less than that of liquid water.

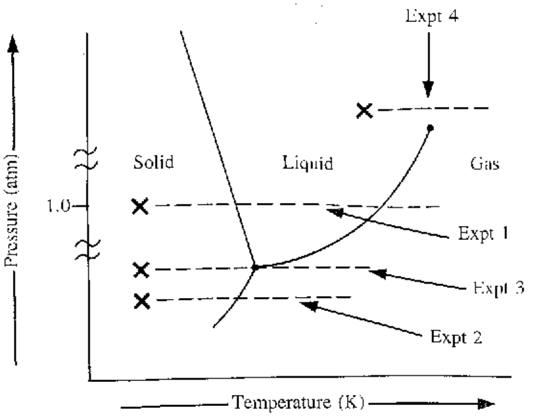


Figure 10.48

Diagrams of various heating experiments on samples of water in a closed system.

the piston exerting a pressure of 1 atm directly on the ice (there is no air space). Since at temperatures below 0°C the vapor pressure of ice is less than 1 atm—which is the constant external pressure on the piston—no vapor is present in the cylinder. As the cylinder is heated, ice is the only component until the temperature reaches 0°C, where the ice changes to liquid water as energy is added. This is the normal melting point of water. When the solid has completely changed to liquid, the temperature again rises. At this point, the cylinder contains only liquid water. *No vapor is present* because the vapor pressure of liquid water under these conditions is less than 1 atmosphere, the constant external pressure on the piston. Heating continues until the temperature of the liquid water reaches 100°C. At this point, the vapor pressure of liquid water is 1 atm, and boiling occurs, with the liquid changing to vapor. This is the normal boiling point of water. After the liquid has been completely converted to steam, the temperature again rises as the heating continues. The cylinder now contains only water vapor.

Experiment 2. Pressure is 2.0 torr. Again we start with ice as the only component in the cylinder at −20°C. The pressure exerted by the piston in this case is only 2.0 torr. As heating proceeds, the temperature rises to −10°C, where the ice changes directly to vapor, a process called sublimation. Sublimation occurs when the vapor pressure of ice is equal to the external pressure, which in this case is only 2.0 torr. No liquid water appears under these conditions because the vapor pressure of liquid water is always greater than 2.0 torr and thus it cannot exist at this pressure. If liquid water were placed in a cylinder under such a low pressure, it would vaporize immediately.

Experiment 3. Pressure is 4.588 torr. Again we start with ice as the only component in the cylinder at −20°C. In this case the pressure exerted on the ice by the piston is 4.588 torr. As the cylinder is heated, no new phase appears until the temperature reaches 0.0098°C. At this point, called the **triple point,** solid and liquid water have identical vapor pressures of 4.588 torr. Thus *at 0.0098°C and 4.588 torr all three states of water are present.* In fact, *only* under these conditions can all three states of water coexist.

Experiment 4. Pressure is 225 atm. In this experiment we start with liquid water in the cylinder at 300°C; the pressure exerted by the piston on the water is 225 atm. Liquid water can be present at this temperature because of the high external pressure. As the temperature increases, something happens that we did not see in the first three experiments: the liquid gradually changes into a vapor but goes through an intermediate "fluid" region, which is neither true liquid nor vapor. This is quite unlike the behavior at lower temperatures and pressures, say at 100°C and 1 atm, where the temperature remains constant while a definite phase change from liquid to vapor occurs. This unusual behavior occurs because the conditions are beyond the critical point for water. The **critical temperature** can be defined as the temperature above which the vapor cannot be liquefied no matter what pressure is applied. The **critical pressure** is the pressure required to produce liquefaction *at* the critical temperature. Together, the critical temperature and the critical pressure define the **critical point.** For water the critical point is 374°C and 218 atm. Note that the liquid/vapor line on the phase diagram for water ends at the critical point. Beyond this point the transition from one state to another involves the intermediate "fluid" region just described.

Applications of the Phase Diagram for Water

There are several additional interesting features of the phase diagram for water. Note that the solid/liquid boundary line has a negative slope. This means that the melting point of water *decreases* as the external pressure *increases.* This behavior, which is opposite to that observed for most substances, occurs because the density of ice is *less* than that of liquid water at the melting point. The maximum density of water occurs at 4°C; when liquid water freezes, its volume increases.

We can account for the effect of pressure on the melting point of water using the following reasoning. At the melting point, liquid and solid water coexist—they are in dynamic equilibrium, since the rate at which ice is melting is just balanced by the rate at which the water is freezing. What happens if we apply pressure to this system? When subjected to increased pressure, matter reduces its volume. This behavior is most dramatic for gases but also occurs for condensed states. Since a given mass of ice at 0°C has a larger volume than the same mass of liquid water, the system can reduce its volume in response to the increased pressure by changing to liquid. Thus, at 0°C and an external pressure greater than 1 atm, water is liquid. In other words, the freezing point of water is less than 0°C when the pressure is greater than 1 atm.

Figure 10.49 illustrates the effect of pressure on ice. At the point X on the phase diagram, ice is subjected to increased pressure at constant temperature. Note that as the pressure is increased, the solid/liquid line is crossed, indicating that the ice melts. This is exactly what happens in ice skating. The narrow blade of the skate exerts a large pressure, since the skater's weight is supported by the small area of the blade. The ice under the blade melts because of the pressure, providing lubrication. After the blade passes, the liquid refreezes, as normal pressure returns. With-

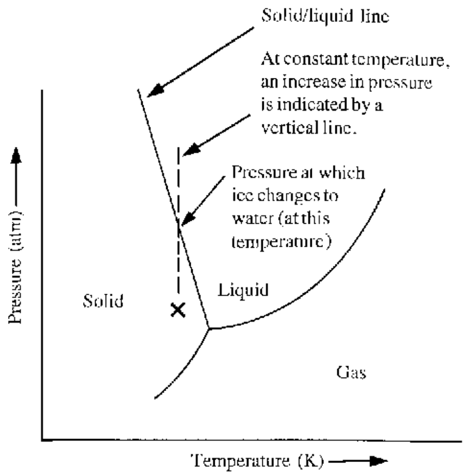


Figure 10.49

The phase diagram for water. At point *x* on the phase diagram, water is a solid. However, as the external pressure is increased while the temperature remains constant (indicated by the vertical dotted line), the solid/liquid line is crossed and the ice melts.

out this lubrication effect due to the thawing ice, ice skating would not be the smooth, graceful activity that it can be.

Ice's lower density has other implications. When water freezes in a pipe or an engine block, it will expand and break the container. This is why water pipes are insulated in cold climates and antifreeze is used in water-cooled engines. The lower density of ice also means that ice formed on rivers and lakes will float, providing a layer of insulation that helps prevent bodies of water from freezing solid in the winter. Aquatic life can therefore continue to live through periods of freezing temperatures.

A liquid boils at the temperature where the vapor pressure of the liquid equals the external pressure. Thus the boiling point of a substance, like the melting point, depends on the external pressure. This is why water boils at different temperatures at different elevations (see Table 10.7), and any cooking carried out in boiling water will be affected by this variation. For example, it takes longer to hard-boil an egg in Leadville, Colorado (elevation: 10,150 ft), than in Chicago (sea level), since water boils at a lower temperature in Leadville.

Water boils at 89°C in Leadville, Colorado.

Boiling Point of Water at Various Locations

Location	Feet above sea level	P_{atm} (torr)	Boiling point (°C)
Top of Mt. Everest, Tibet	29,028	240	70
Top of Mt. McKinley, Alaska	20,320	340	79
Top of Mt. Whitney, Calif.	14,494	430	85
Leadville, Colo.	10,150	510	89
Top of Mt. Washington, N.H.	6,293	590	93
Boulder, Colo.	5,430	610	94
Madison, Wis.	900	730	99
New York City, N.Y.	10	760	100
Death Valley, Calif.	−282	770	100.3

Table 10.7

As we mentioned earlier, the phase diagram for water describes a closed system. Therefore, we must be very cautious in using the phase diagram to explain the behavior of water in a natural setting, such as on the earth's surface. For example, in dry climates (low humidity), snow and ice seem to sublime—a minimum amount of slush is produced. Wet clothes put on an outside line at temperatures below 0°C freeze, then dry while frozen. However, the phase diagram (Fig. 10.47) shows that ice should *not* be able to sublime at normal atmospheric pressures. What is happening in these cases? Ice in the natural environment is not in a closed system. The pressure is provided by the atmosphere rather than by a solid piston. This means that the vapor produced over the ice can escape from the immediate region as soon as it is formed. The vapor does not come to equilibrium with the solid, and the ice slowly disappears. Sublimation, which seems forbidden by the phase diagram, does in fact occur under these conditions.

The Phase Diagram for Carbon Dioxide

The phase diagram for carbon dioxide (Fig. 10.50) differs from that for water. The solid/liquid line has a positive slope, since solid carbon dioxide is more dense than liquid carbon dioxide. The triple point for carbon dioxide occurs at 5.1 atm and −56.6°C, and the critical point occurs at 72.8 atm and 31°C. At a pressure of 1 atm, solid carbon dioxide sublimes at −78°C, a property that leads to its common name, *dry ice*. No liquid phase occurs under normal atmospheric conditions, making dry ice a convenient refrigerant.

Carbon dioxide is often used in fire extinguishers, where it exists as a liquid at 25°C under high pressures. Liquid carbon dioxide released from the extinguisher into the environment at 1 atm immediately changes to a vapor. Being heavier than air, this vapor smothers the fire by keeping oxygen away from the flame. The liquid/vapor transition is highly endothermic, so cooling also results, which helps to put out the fire. The "fog" produced by a carbon dioxide extinguisher is not solid carbon dioxide but rather moisture frozen from the air.

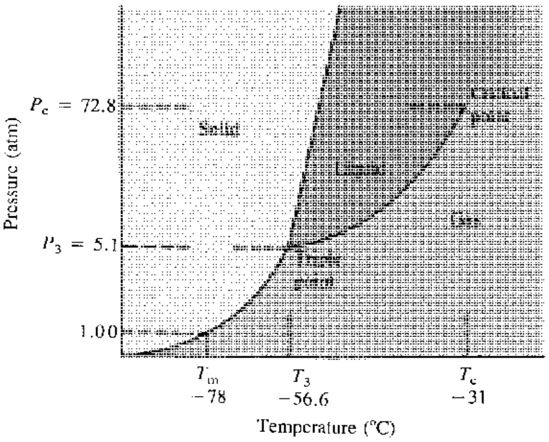


Figure 10.50

The phase diagram for carbon dioxide. The liquid state does not exist at a pressure of 1 atmosphere. The solid/liquid line has a positive slope since the density of solid carbon dioxide is greater than that of liquid carbon dioxide.

TRANSISTORS AND PRINTED CIRCUITS

Transistors have had an immense impact on the technology of electronic devices for which signal amplification is needed, such as communications equipment and computers. Before the invention of the transistor at Bell Laboratories in 1947, amplification was provided exclusively by vacuum tubes, which were both bulky and unreliable. The first electronic digital computer, ENIAC, built at the University of Pennsylvania, had 19,000 vacuum tubes and consumed 150,000 watts of electricity. Because of the discovery and development of the transistor and the printed circuit, a hand-held calculator run by a small battery has the same computing power as ENIAC.

A *junction transistor* is made by joining n-type and p-type semiconductors so as to form an n-p-n or a p-n-p junction. The former type is shown in Fig. 10.51. In this diagram the input signal (to be amplified) occurs in circuit 1 which has a small resistance and a forward-biased n-p junction (junction 1). As the voltage of the input signal to this circuit varies, the current in the circuit varies, which means there is a change in the number of electrons crossing the n-p junction. Circuit 2 has a relatively large resistance and is under reverse bias. The key to the operation of the transistor is that current only flows in circuit 2 when electrons crossing junction 1 also cross junction 2 and travel to the positive terminal. Since the current in circuit 1 determines the number of electrons crossing junction 1, the number of electrons available to cross junction 2 is also directly proportional to the current in circuit 1. The current in circuit 2 therefore varies depending on the current in circuit 1.

The voltage (V), current (I), and resistance (R) in a circuit are related by the equation

$$V = IR$$

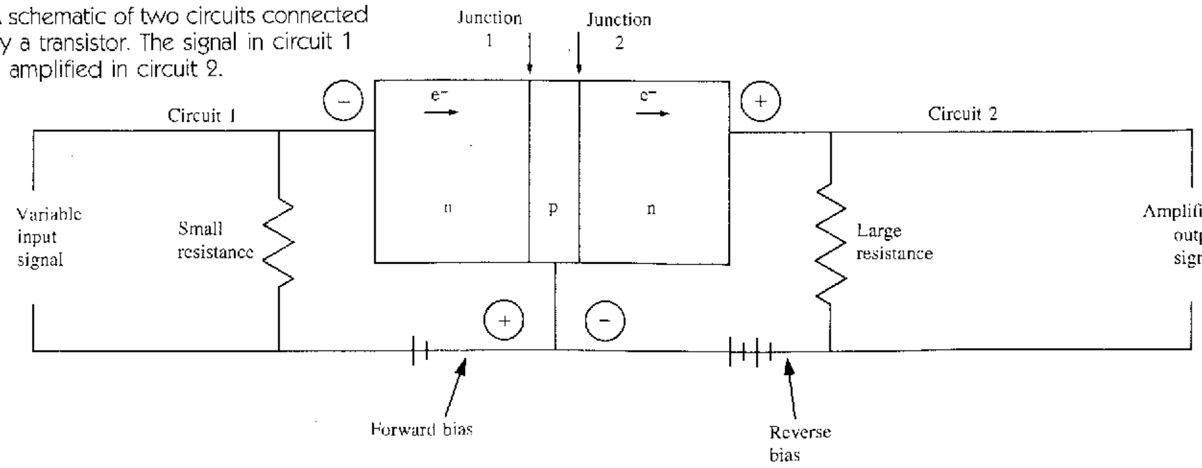
Since circuit 2 has a large resistance, a given current in circuit 2 produces a larger voltage than the same current in circuit 1, which has a small resistance. Thus a signal of variable voltage in circuit 1, such as might be produced by a human voice on a telephone, is reproduced in circuit 2, but with much greater voltage changes. That is, the input signal has been *amplified* by the junction transistor. This device can do the job of the large vacuum tube and yet is a tiny component of a printed circuit on a silicon chip.

Silicon chips are really "planar" transistors constructed from thin layers of n-type and p-type regions connected by conductors. A tiny chip less than 1 cm wide can contain several hundred printed circuits and be used in computers, calculators, radios, and television sets.

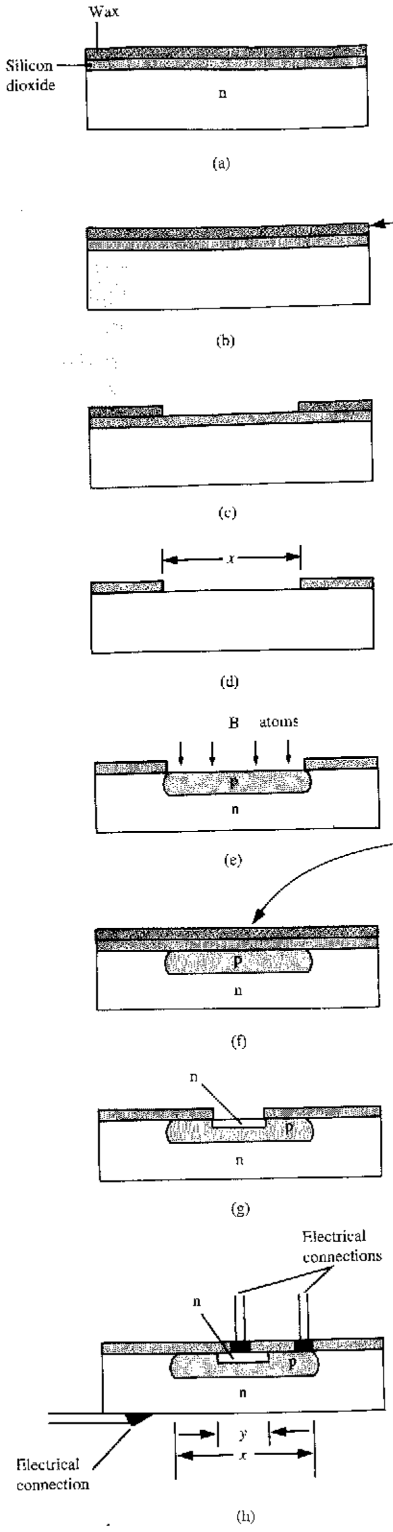
A printed circuit has many n-p-n junction transistors. Figure 10.52 illustrates the formation of one transis-

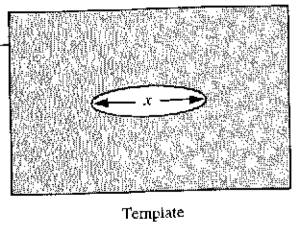
Figure 10.51

A schematic of two circuits connected by a transistor. The signal in circuit 1 is amplified in circuit 2.



CHEMICAL IMPACT





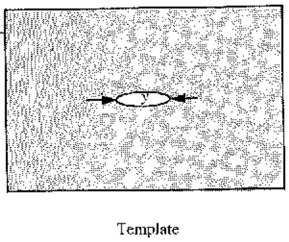


Figure 10.52

The steps for forming a transistor in a crystal of initially pure silicon.

tor area. The chip begins as a thin wafer of silicon that has been doped with an n-type impurity. A protective layer of silicon oxide is then produced on the wafer by exposing it in a furnace to an oxidizing atmosphere. The next step is to produce a p-type semiconductor. To do this, the surface of the oxide is covered by a light-sensitive wax, as shown in Fig. 10.52(a). A template that only allows light to shine through in selected areas is then placed on top [Fig. 10.52(b)], and light is shone on the chip. The wax that has been exposed to light undergoes a chemical change that causes its solubility to be different from the unexposed wax. The unexposed wax is then dissolved using selective solvents [Fig. 10.52(c)], and the exposed area is treated with an etching solution to dissolve the oxide coating [Fig. 10.52(d)]. When the remaining wax is dissolved, the silicon wafer has its oxide coating intact except at the one spot (of diameter *x*), as shown in Fig. 10.52(d).

Exposing the wafer to a p-type impurity such as boron at about 1000°C causes a p-type semiconductor area to be formed in the exposed spot as the boron atoms diffuse into the silicon crystal [Fig. 10.52(e)]. Next, to form a small n-type area in the center of the p-type region, the wafer is again placed in the oxidizing furnace to be recoated over its entire surface with oxide. Then a new wax covering is applied, which is illuminated through a template with a transparent area indicated by *y* [Fig. 10.52(f)]. The wax and oxide are then removed from the illuminated area, and the wafer is exposed to an n-type impurity to form a small n-type region as shown in Fig. 10.52(g). Next, conductors are layered onto the chip giving the finished transistor [Fig. 10.52(h)], which has two circuits connected through an n-p-n junction, such as is illustrated in Fig. 10.51. This transistor then becomes a part of a larger circuit layered onto the chip and interconnected by conductors.

The method given here for producing a printed circuit does not represent the latest technology in this field. The manufacture of printed circuits is a highly competitive business and changes in methodology occur almost daily.

Summary

Liquids and solids are the two condensed states of matter; their formation is caused by intermolecular forces among the molecules, atoms, or ions. Dipole-dipole forces are attractions between molecules that have dipole moments. These forces are particularly strong for molecules containing hydrogen bonded to a highly electronegative element such as nitrogen, oxygen, or fluorine. In these cases the resulting dipole forces are called hydrogen bonds and account for the unusually high boiling points of the hydrides of the first elements in Groups 4A, 5A, 6A, and 7A. London dispersion forces caused by instantaneous dipoles are important in substances composed of nonpolar molecules. Liquids exhibit various properties—surface tension, capillary action, and viscosity—that depend on the strengths of the intermolecular forces.

The two broadest categories of solids are crystalline and amorphous solids. Crystalline solids have a regular arrangement, or lattice, of component particles, the smallest repeating unit of which is the unit cell. The arrangement of particles in a crystalline solid can be determined by X-ray diffraction techniques, and the interatomic distances in the crystal can be related to the wavelength and angle of reflection of the X rays by the Bragg equation.

The structure of metals is modeled by assuming atoms to be uniform spheres and packing them as compactly as possible. There are two closest packing arrangements: hexagonal and cubic.

The bonding in metallic crystals can be described in terms of the electron sea model (valence electrons are assumed to move freely about the metal cations) or in terms of the band model (electrons are assumed to travel through the metal crystal in molecular orbitals formed from the valence atomic orbitals of the metal atoms). In the band model the large number of available atomic orbitals form closely spaced energy levels. Electricity can be readily conducted by electrons in conduction bands, which are molecular orbitals containing only a single electron.

Metals form alloys, which can be classified as substitutional or interstitial.

Carbon is a typical network solid containing strong directional covalent bonds. Diamond and graphite are the two allotropes of carbon, with very different physical properties determined by their different bonding.

Silicon should be very similar in properties to carbon since carbon and silicon are next to each other in Group 4A, but in fact their compounds are markedly dissimilar. Silica, the fundamental silicon-oxygen compound, does not contain discrete SiO_2 molecules but rather a network of interconnected SiO_4 tetrahedra. Silicates, salts containing polyatomic anions of silicon and oxygen, are components of rocks, soil, clay, glass, and ceramics.

Semiconductors are formed when pure silicon is doped with other elements. An n-type semiconductor contains atoms with more valence electrons than the silicon atom, and a p-type semiconductor has atoms with fewer valence electrons than silicon. The modern electronics industry is based on devices that contain p-n junctions.

Molecular solids consist of discrete molecular units held together by relatively weak intermolecular forces. Ice is an example. Ionic solids, on the other hand, are held together by strong electrostatic attractions. The crystal structure of ionic solids can often be described by fitting the smaller ions (usually cations) into holes in the closest packed structures formed by the larger ions (usually anions).

The phase change between liquid and vapor is called vaporization, or evaporation, and the energy required to change 1 mole of liquid to its vapor is the heat of vaporization (ΔH_{vap}). Condensation is the reverse process by which vapor molecules return to the liquid state. When the rates of evaporation and condensation exactly balance in a closed container, the system is at equilibrium, and the resulting pressure of the vapor is called the vapor pressure.

Volatility of liquids depends on both molecular weight and intermolecular forces. Liquids composed of heavier molecules tend to be less volatile, as do liquids with strong intermolecular forces. The normal melting point of a solid is defined as the temperature at which the solid and its liquid have identical vapor pressures. The normal boiling point of a liquid occurs at a temperature where the vapor pressure of the liquid is 1 atmosphere.

A phase diagram for a substance shows which state exists at a given temperature and pressure. The triple point on a phase diagram represents the temperature and pressure where all three states coexist. The critical point is defined by the critical temperature and critical pressure. Critical temperature is that temperature above which the vapor cannot be liquefied no matter what pressure is applied. The critical pressure is the pressure required to produce liquefaction at the critical temperature.

Key Terms

condensed states (10.1)
intermolecular forces
dipole-dipole attraction
hydrogen bonding
London dispersion forces
surface tension (10.2)
capillary action
viscosity
crystalline solid (10.3)
amorphous solid
lattice
unit cell
X-ray diffraction
ionic solid
molecular solid
atomic solid
closest packing (10.4)
hexagonal closest packed (hcp) structure
cubic closest packed (ccp) structure
electron sea model
band model
bands
conduction band
alloy
substitutional alloy
interstitial alloy
network solid (10.5)
silica
silicate
glass
ceramic
semiconductor
n-type semiconductor
p-type semiconductor
p-n junction
vaporization (10.8)
heat of vaporization
condensation
vapor pressure
sublimation
heating curve
normal melting point
heat of fusion
normal boiling point
supercooled
superheated
phase diagram (10.9)
triple point
critical temperature
critical pressure
critical point

Exercises

Intermolecular Forces and Physical Properties

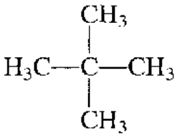
1. Describe the relationship between the polarity of individual molecules and the nature and strength of intermolecular forces.
2. List the major types of intermolecular forces in order of increasing strength. Is there some overlap? That is, can the strongest London dispersion forces be greater than some dipole-dipole forces? Give examples of such instances.
3. Describe the relationship between molecular size and the strength of London dispersion forces.
4. How do the following physical properties depend on the strength of intermolecular forces?
   a. surface tension
   b. viscosity
   c. melting point
   d. boiling point
   e. vapor pressure
5. Does the nature of intermolecular forces change when a substance goes from a solid to a liquid, or from a liquid to a gas? What causes a substance to undergo a phase change?

6. Identify the most important types of interparticle forces present in the solids of each of the following substances:

a. $BaSO_4$
b. H_2S
c. Xe
d. C_2H_6
e. Cs
f. Hg
g. P_4
h. H_2O
i. NH_4Cl
j. steel
k. teflon, $CF_3(CF_2CF_2)_nCF_3$
l. polyethylene, $CH_3(CH_2CH_2)_nCH_3$
m. $CHCl_3$
n. Ge
o. NO
p. BF_3

7. Rationalize the difference in boiling points for each of the following pairs of substances:

a. *n*-pentane $CH_3CH_2CH_2CH_2CH_3$ 36.2°C
neopentane 9.5°C



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$$

b. dimethyl ether CH_3OCH_3 35°C
ethanol CH_3CH_2OH 79°C
c. HF 20°C
HCl −85°C
d. $TiCl_4$ 136°C
LiCl 1360°C
e. HCl −85°C
LiCl 1360°C
f. LiCl 1360°C
CsCl 1290°C

8. Rationalize the following differences in physical properties in terms of intermolecular forces. Compare the first three substances to each other, compare the last three to each other, and then compare all six. Can you account for any anomalies?

	bp (°C)	mp (°C)	ΔH_{vap}(kJ/mol)
Benzene, C_6H_6	80	6	33.9
Naphthalene, $C_{10}H_8$	218	80	51.5
Carbon tetrachloride	76	−23	31.8
Acetone, CH_3COCH_3	56	−95	31.8
Acetic acid, CH_3CO_2H	118	17	39.7
Benzoic acid, $C_6H_5CO_2H$	249	122	68.2

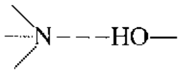
9. Consider the following enthalpy changes:

$$F^- + HF \rightarrow FHF^- \quad \Delta H = -155 \text{ kJ/mol}$$

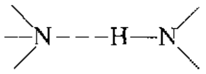
$$(CH_3)_2C{=}O + HF \rightarrow (CH_3)_2C{=}O{-}{-}{-}HF \quad \Delta H = -46 \text{ kJ/mol}$$

$$H_2O(g) + HOH(g) \rightarrow H_2O{-}{-}{-}HOH \text{ (in ice)} \quad \Delta H = -21 \text{ kJ/mol}$$

How do the strengths of hydrogen bonds vary with the electronegativity of the element to which hydrogen is bonded? Where in the above series would you expect hydrogen bonds of the following type to fall?



and



10. What structure would you predict for the bifluoride ion (FHF^-)? Why?

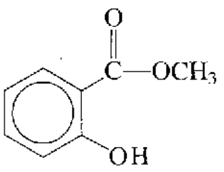
11. Why is ΔH_{vap} for water much greater than ΔH_{fus}? What does this say about changes in intermolecular forces in going from liquid to solid to vapor?

12. Using the heats of fusion and vaporization for water, calculate the change in enthalpy for the sublimation of water:

$$H_2O(s) \rightarrow H_2O(g)$$

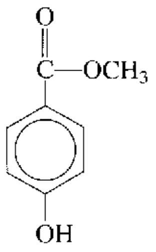
Using the ΔH value given in Exercise 9 and the number of hydrogen bonds formed to each water molecule, estimate what portion of the intermolecular forces in ice can be accounted for by hydrogen bonding.

13. Oil of wintergreen, or methyl salicylate, has the following structure:



mp = −8°C

Methyl-4-hydroxybenzoate is another molecule with exactly the same molecular formula; it has the following structure:



mp = 127°C

Account for the large difference in the melting points of the two substances.

14. Consider the following melting point data:

Compound	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	SCl_2	Cl_2
mp (°C)	801	708	190	−70	−91	−78	−101
Compound	NaF	MgF_2	AlF_3	SiF_4	PF_5	SF_6	F_2
mp (°C)	997	1396	1040	−90	−94	−56	−220

Account for the trends in melting points in terms of interparticle forces.

15. In each of the following groups of substances, pick the one that has the given property. Justify each answer.
a. Highest boiling point: Hg, NaCl, or N_2
b. Smallest surface tension: H_2O, CH_3CN, or CH_3OH
c. Lowest freezing point: H_2, CH_4, or CO
d. Smallest vapor pressure at 25°C: SiO_2, CO_2, or H_2O
e. Greatest viscosity: $CH_3CH_2CH_2CH_3$, CH_3CH_2OH, or $HOCH_2CH_2OH$
f. Strongest hydrogen bonding: NH_3, PH_3, or SbH_3
g. Greatest heat of vaporization: HF, HCl, HBr, or HI
h. Smallest enthalpy of fusion: H_2O, CO_2, MgO, or Li_2O

16. The heats of vaporization of the hydrogen halides are

HF	7.5 kJ/mol
HCl	16.1 kJ/mol
HBr	17.6 kJ/mol
HI	19.7 kJ/mol

The boiling points for the hydrogen halides follow the same trend as those of the hydrides of the elements in Group 5 and Group 6. Can you account for any discrepancies between these data and your predictions in part g of Exercise 15? *Hint:* Think about the effects of aggregates in the vapor phase.

17. How could you tell experimentally if TiO_2 is an ionic solid or a network solid? What would you predict on the basis of electronegativity differences?

18. Distinguish between each of the following:
a. polarizability and polarity
b. London dispersion forces and dipole-dipole forces
c. intermolecular forces and intramolecular forces

19. Titanium(IV) chloride is a liquid that boils at 136°C. What might explain why $TiCl_4$ exists as discrete covalent molecules rather than as an ionic substance?

Properties of Liquids

20. In what ways are liquids similar to solids? In what ways are liquids similar to gases?

21. Define critical temperature and critical pressure. In terms of the kinetic molecular theory, why is it impossible for a substance to exist as a liquid above its critical temperature?

22. What is the relationship between critical temperature and intermolecular forces?

23. The shape of the meniscus of water in a glass tube is different from that of mercury in a glass tube. Why?

H_2O in glass

Hg in glass

What would be the shape of the meniscus of water in a polyethylene tube? (Polyethylene can be represented as $CH_3(CH_2)_nCH_3$ where n is a large number on the order of 1000.)

24. Will water rise to a greater height by capillary action in a glass tube or in a polyethylene tube of the same diameter?

25. Some of the physical properties of H_2O and D_2O are as follows:

	H_2O	D_2O
Density at 20°C (g/mL)	0.997	1.108
Boiling point (°C)	100.00	101.41
Melting point (°C)	0.00	3.79
ΔH_{vap} (kJ/mol)	40.7	41.61
ΔH_{fus} (kJ/mol)	6.01	6.3

Account for the differences. (Note: D is a symbol often used for ^2H, the deuterium isotope of hydrogen.)

26. Hydrogen peroxide (H_2O_2) is a syrupy liquid with a relatively low vapor pressure and a normal boiling point of 152.2°C. Rationalize the differences of these physical properties from those of water.

Structures and Properties of Solids

27. Distinguish between the following pairs:
a. crystalline solid and amorphous solid
b. ionic solid and molecular solid
c. molecular solid and network solid

28. Will a crystalline solid or an amorphous solid give a simpler X-ray diffraction pattern? Why?

29. When a metal was exposed to X rays, it emitted X rays of a different wavelength. The emitted X rays were diffracted by a LiF crystal (d = 201 pm) and first-order diffraction (n = 1 in the Bragg equation) was detected at an angle of 34.68°. Calculate the wavelength of the X ray emitted by the metal.

30. The value of $2d$ for mica, a silicate mineral, is 19.93 Å. What would be the angle for first-order diffraction ($n = 1$ in the Bragg equation) of X rays from a molybdenum X-ray source ($\lambda = 0.712$ Å)?

31. X rays from a copper X-ray tube ($\lambda = 1.54$ Å) were diffracted at an angle of 14.22° by a crystal of silicon. Assuming first-order diffraction ($n = 1$ in the Bragg equation), what is the interplanar spacing in silicon?

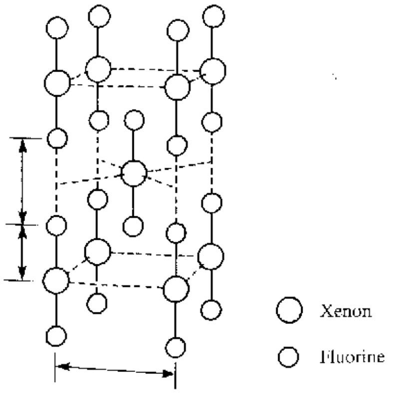
32. Consider the following values for lattice energies (Section 8.5) and interionic distances (center to center) for some of the alkali metal halides:

	Lattice energy (kJ/mol)	Interionic distance (Å)
LiF	1034	2.01
LiCl	840	2.57
LiBr	781	2.75
LiI	718	3.02
NaF	914	2.31
NaCl	770	2.81
NaBr	728	2.98
NaI	680	3.23
KCl	701	3.14
RbCl	682	3.28
CsCl	629	3.56
CsF	744	3.00

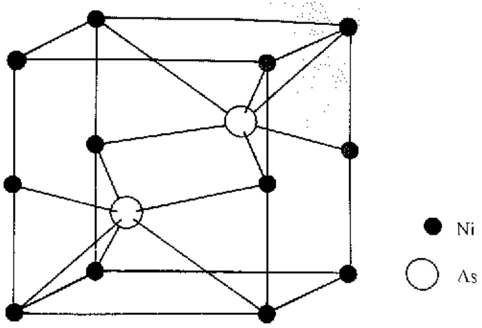
Plot the lattice energies of these compounds as a function of interionic distance and as a function of the reciprocal of the interionic distance. Which plot is most nearly linear? Why? Are there any discrepancies in the linear plot? Account for them.

33. A metallic solid with atoms in a face-centered cubic unit cell with an edge length of 3.92 Å has a density of 21.45 g/cm^3. Calculate the atomic weight and the atomic radius of the metal. What element might this metal be?

34. The unit cell for a pure xenon fluoride is shown below. What is the formula of the compound?



35. The unit cell for nickel arsenide is shown below. What is the formula of this compound?

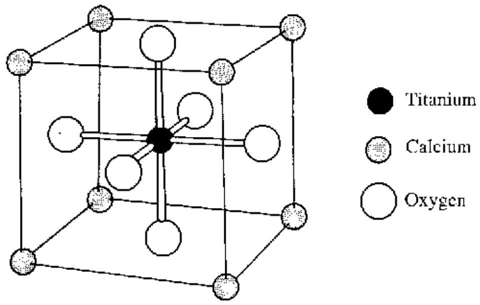


36. Cobalt exists in two crystalline forms. Below 417°C cobalt is in the α-form, which has a hexagonal closest packed structure and a density of 8.90 g/cm^3. Above 417°C cobalt is in the β-form, a cubic closest packed arrangement. The atomic radius of cobalt is 1.25 Å. Is there a change in the density of cobalt in going from the α-form to the β-form?

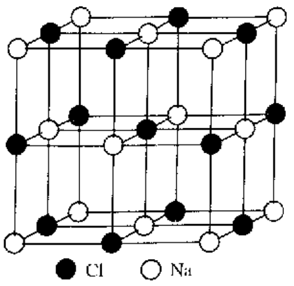
37. Iridium (Ir) has a face-centered cubic unit cell with an edge length of 3.833 Å. The density of iridium is 22.61 g/cm^3. Use these data to calculate a value for Avogadro's number.

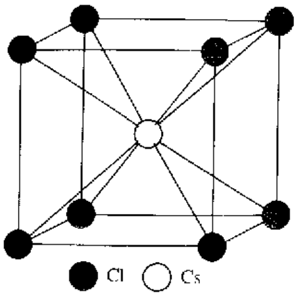
38. Titanium metal has a body-centered cubic unit cell. The density of titanium is 4.50 g/cm^3. Calculate the edge length of the unit cell and a value for the atomic radius of titanium. (Hint: In a body-centered arrangement of spheres, the spheres touch across the body diagonal.)

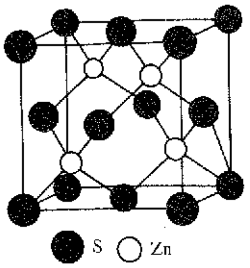
39. Perovskite is a mineral containing calcium, titanium, and oxygen. A diagram of its unit cell is shown below. What is the formula of perovskite?

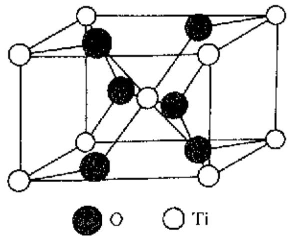


40. The structures of some common crystalline substances are shown below. Show that the net composition of each unit cell corresponds to the correct formula of each substance.









41. Nickel has a face-centered cubic unit cell. The density of nickel is 6.84 g/cm^3. Calculate a value for the atomic radius of nickel.

42. Tungsten has the highest melting point of all the metals. Carbon is the only element with a higher melting point. The atomic radius of tungsten is 1.39 Å, and it has a density of 19.3 g/cm^3. Does tungsten have a body-centered or face-centered cubic unit cell?

43. Use the band model to describe differences among insulators, conductors, and semiconductors.

44. Use the band model to explain why each of the following increases the conductivity of a semiconductor:
   a. increasing the temperature
   b. irradiating with light
   c. adding an impurity

Phase Changes and Phase Diagrams

45. Define each of the following:
   a. condensation
   b. evaporation
   c. sublimation
   d. supercooled liquid

46. Describe what is meant by a dynamic equilibrium in terms of the vapor pressure of a volatile liquid.

47. The temperature inside a pressure cooker is 115°C. Use Equation 10.5 to calculate the vapor pressure of water inside the pressure cooker. What would be the temperature inside the pressure cooker if the vapor pressure of water was 3.5 atm.?

48. What pressure would have to be applied to steam at 350°C to condense the steam to liquid water?

49. How much energy does it take to convert 500 g of ice at −20°C to steam at 250°C? (Heat capacities: ice, 2.1 J/g °C; liquid, 4.2 J/g °C; steam, 1.8 J/g °C; $\Delta H_{\text{vap}} = 41.2$ kJ/mol, $\Delta H_{\text{fus}} = 6.0$ kJ/mol.)

50. What is the final temperature when 850 J of energy is added to 10.0 g ice at 0°C?

51. In regions with dry climates, evaporative coolers are used to cool air. A typical electric air conditioner is rated at 10,000 Btu/hr (1 Btu, or British thermal unit = amount of energy to raise the temperature of 1 lb of water by 1°F.). How much water must be evaporated each hour to dissipate this much heat?

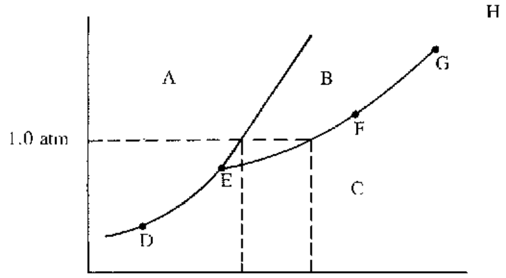
52. Plot the following data and determine ΔH_{vap} for magnesium and lithium. In which metal is the bonding stronger?

Vapor pressure (mm Hg)	Temperature (°C)	
	Li	Mg
1	750	620
10	890	740
100	1080	900
400	1240	1040
760	1310	1110

53. How does each of the following affect the rate of evaporation of a liquid in an open dish?
   a. intermolecular forces
   b. temperature
   c. surface area

54. Some water is placed in a sealed glass container connected to a vacuum pump (a device used to pump gases from a container), and the pump is turned on. The water appears to boil and then freezes. Explain these changes using the phase diagram for water. What would happen to the ice if the vacuum pump was left on indefinitely?

55. Consider the phase diagram given below. What phases are present at points A through H? Identify the triple point, normal boiling point, normal freezing point, and critical point.



56. Describe how a phase diagram can be constructed from the heating curve for a substance.

57. A substance has the following properties.

		Heat capacities	
ΔH_{vap}	20 kJ/mol	$C_{(s)}$	3.0 J/g °C
ΔH_{fus}	5 kJ/mol	$C_{(l)}$	2.5 J/g °C
bp	75°C	$C_{(g)}$	1.0 J/g °C
mp	−15°C		

Sketch a heating curve for the substance starting at −50°C.

58. Why is a burn from steam typically much more severe than a burn from boiling water?

59. A 10.0-g chunk of sodium metal is dropped into a mixture of 50.0 g of water and 50.0 g of ice at 0°C. The reaction is as follows

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) \qquad \Delta H = -368 \text{ kJ}$$

Will the ice melt? Assuming that the final mixture has a heat capacity of 4.18 J/g °C calculate the final temperature.

Additional Exercises

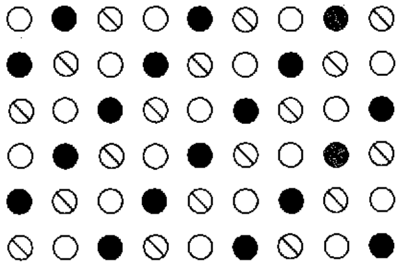
60. Boron nitride (BN) exists in two forms. The first is a slippery solid formed from the reaction of BCl_3 with NH_3, followed by heating in an ammonia atmosphere at 750°C. Subjecting the first form of BN to a pressure of 85,000 atm at 1800°C produces a second form that is the second hardest substance known. Both forms of BN remain solids to 3000°C. Suggest structures for the two forms of BN.

61. A crystal of hafnium (Hf) was exposed to X rays from a Mo X-ray tube (λ = 71.2 pm). First-order diffraction (n = 1 in the Bragg equation) was observed at an angle of 5.564°. The density of hafnium is 13.28 g/cm^3. Assuming that the distance calculated from the Bragg equation gives the edge length of the cubic unit cell, does hafnium exist in a body-centered or face-centered cubic arrangement? Calculate the atomic radius of hafnium.

62. From the following data for liquid nitric acid, determine its heat of vaporization and normal boiling point.

Temperature (°C)	Vapor pressure (mm Hg)
0	14.4
10	26.6
20	47.9
30	81.3
40	133
50	208
80	670

63. What is the unit cell for the following two-dimensional array of circles? How many of each type of circle are in each unit cell?

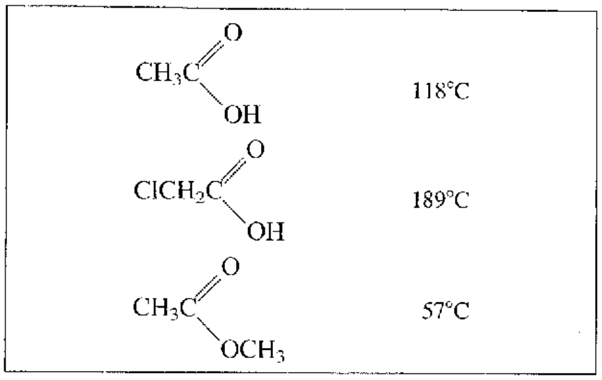


64. When wet laundry is hung on a clothesline on a cold winter day, it will freeze, but eventually dry. Explain.

65. What fraction of the total volume of a cubic closest packed structure is occupied by atoms?

66. Many organic acids, such as acetic acid (CH_3CO_2H), whose structure is shown in Exercise 67, exist in the gas phase as hydrogen-bonded dimers (two molecule units). Draw a reasonable structure for such dimers.

67. Rationalize the following boiling points:



68. Use the diagram of the unit cell for the hexagonal closest packed structure in Fig. 10.14 to calculate the net number of atoms in the unit cell.

CHAPTER EIGHT

Bonding—General Concepts

CONTENTS

As we examine the world around us, we find it to be composed almost entirely of compounds and mixtures of compounds: rocks, coal, soil, petroleum, trees, and human bodies are all complex mixtures of chemical compounds in which different kinds of atoms are bound together. Substances composed of unbound atoms do exist in nature, but they are very rare. Examples are the argon in the atmosphere and the helium mixed with natural gas reserves.

The manner in which atoms are bound together has a profound effect on chemical and physical properties. For example, graphite is a soft, slippery material used as a lubricant in locks, and diamond is one of the hardest materials known, valuable both as a gemstone and in industrial cutting tools. Why do these materials, both composed solely of carbon atoms, have such different properties? The answer, as we will see, lies in the bonding in these substances.

Silicon and carbon are next to each other in Group 4A on the periodic table. From our knowledge of periodic trends, we might expect SiO_2 and CO_2 to be very similar. But SiO_2 is the empirical formula of silica, which is found in sand and quartz, and carbon dioxide is a gas, a product of respiration. Why are they so different? We will be able to answer this question after we have developed models for bonding.

Molecular bonding and structure play the central role in determining the course of all chemical reactions, many of which are vital to our survival. Later in this book we will demonstrate their importance by showing how enzymes facilitate complex chemical reactions, how genetic characteristics are transferred, and how hemoglobin in the blood carries oxygen throughout the body. All of these fundamental biological reactions hinge on the geometric structures of molecules, sometimes depending on very subtle differences in molecular shape to channel the chemical reaction one way rather than another.

Many of the world's current problems require fundamentally chemical answers: disease and pollution control, the search for new energy sources, the development of new fertilizers to increase crop yields, the improvement of the protein content in various staple grains, and many more. Clearly, to understand the behavior of natural materials, we must understand the nature of chemical bonding and the factors that control the structures of compounds. In this chapter we will present various classes of compounds that illustrate the different types of bonds. We will then develop models to describe the structure and bonding that characterize materials found in nature. Later these models will be useful in understanding chemical reactions.

8.1 | Types of Chemical Bonds

PURPOSE

- ☐ To explain why an ionic bond is formed.
- ☐ To explain why a covalent bond is formed.
- ☐ To introduce the polar covalent bond.

What is a chemical bond? There is no simple and yet complete answer to this question. In Chapter 2 we defined bonds as forces that hold groups of atoms together and make them function as a unit.

There are many types of experiments we can perform to determine the fundamental nature of materials. For example, we can study physical properties such as melting point, hardness, and electrical and thermal conductivity. We can also study solubility characteristics and the properties of the resulting solutions. To determine the charge distribution in a molecule, we can study its behavior in an electric field. We can obtain information about the strength of a bonding interaction by measuring the energy required to break the bond, the **bond energy.**

There are several ways in which atoms can interact with one another to form aggregates. We will consider several specific examples to illustrate the various types of chemical bonds.

Earlier, we saw that when solid sodium chloride is dissolved in water, the resulting solution conducts electricity, a fact that convinces us that sodium chloride is composed of Na^+ and Cl^- ions. So when sodium and chlorine react to form sodium chloride, electrons are transferred from the sodium atoms to the chlorine atoms to form Na^+ and Cl^- ions, which then aggregate to form solid sodium chloride. Why does this happen? The best simple answer is that *the system can achieve the lowest possible energy by behaving in this way.* The attraction of a chlorine atom for the extra electron and the very strong mutual attractions of the oppositely charged ions provide the driving forces for the process. The resulting solid sodium chloride is a very sturdy material; it has a melting point of approximately 800°C. The bonding forces that produce this great thermal stability result from the electrostatic attractions of the closely packed, oppositely charged ions. This is an example of **ionic bonding.** Ionic substances are formed when an atom that loses electrons relatively easily reacts with an atom that has a high affinity for electrons. In other words, an **ionic compound** results when a metal reacts with a nonmetal.

The energy of interaction between a pair of ions can be calculated using **Coulomb's law:**

$$E = 2.31 \times 10^{-19}\ \text{J nm}\left(\frac{Q_1 Q_2}{r}\right)$$

where E has units of joules, r is the distance between the ion centers in nm, and Q_1 and Q_2 are the numerical ion charges.

For example, in solid sodium chloride the distance between the centers of the Na^+ and Cl^- ions is 2.76 Å (0.276 nm), and the ionic energy per pair of ions is

$$E = 2.31 \times 10^{-19}\ \text{J nm}\left[\frac{(+1)(-1)}{0.276\ \text{nm}}\right] = -8.37 \times 10^{-19}\ \text{J}$$

where the negative sign indicates an attractive force. That is, the *ion pair has lower energy than the separated ions*. For a mole of pairs of Na^+ and Cl^- ions, the energy of interaction is

$$E = \left(-8.37 \times 10^{-19}\ \frac{\text{J}}{\text{ion pair}}\right)\left(6.022 \times 10^{23}\ \frac{\text{ion pair}}{\text{mol}}\right)$$

$$= -504\ \frac{\text{kJ}}{\text{mol}}$$

Coulomb's law can also be used to calculate the repulsive energy when two like-charged ions are brought together. In this case the calculated value of the energy will have a positive sign.

We have seen that a bonding force develops when two very different types of atoms react to form oppositely charged ions. But how does a bonding force develop between two identical atoms? Let's explore this situation from a very simple point of view by considering the energy terms that result when two hydrogen atoms are brought close together, as shown in Fig. 8.1(a). When hydrogen atoms are brought close together, two opposing forces come into play. There are two unfavorable energy terms, proton-proton repulsion and electron-electron repulsion, and one favorable term, proton-electron attraction. Under what conditions will the H_2 molecule be favored over the separated hydrogen atoms? That is, what conditions will favor bond formation? The answer lies in the strong tendency in nature for any system to achieve the lowest possible energy. A bond will form, that is, the two hydrogen atoms will exist as a molecular unit, if the system can lower its total energy in the process.

A bond will form if the energy of the aggregate is lower than that of the separated atoms.

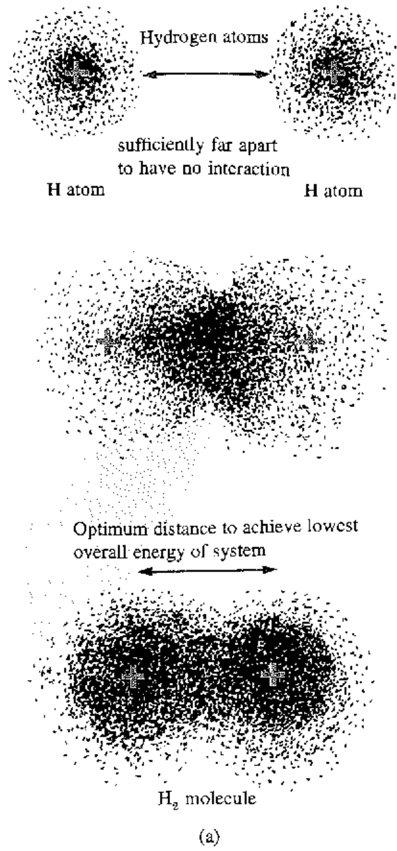
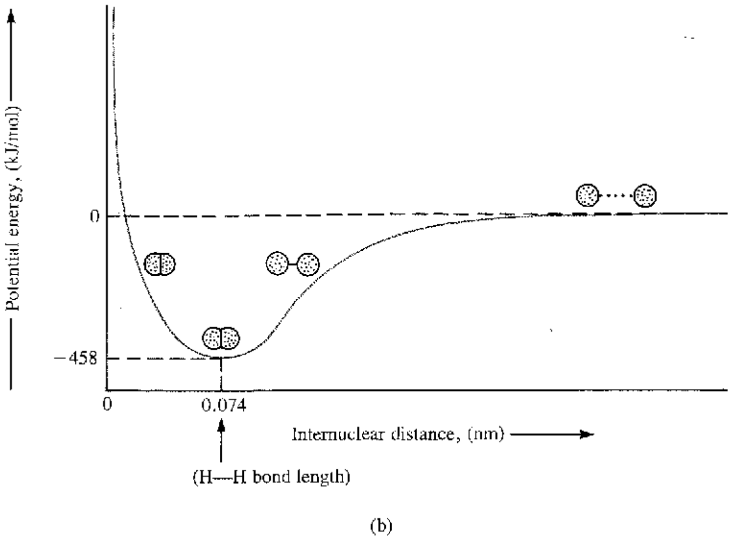


Figure 8.1.

The interaction of two hydrogen atoms. (a) As two hydrogen atoms get close enough to interact, there is an increase in electron probability in the area between the nuclei. The fact that the electrons are simultaneously attracted to two nuclei causes the energy of the H_2 molecule to be lower than that of two separated atoms. A bond results. (b) Potential energy profile as a function of the distance between the nuclei of the hydrogen atoms. As the atoms approach each other, the energy decreases until the distance reaches 0.074 nm (0.74 Å) and then begins to increase again as the atoms get closer due to repulsions.



In this case, then, the hydrogen atoms will position themselves so that the system will achieve the lowest possible energy; the system will act to minimize the sum of the positive (repulsive) energy terms and the negative (attractive) energy term. The distance where the energy is minimum is called the **bond length.** The total energy of this system as a function of distance between the hydrogen nuclei is shown in Fig. 8.1(b). Note several important features of this diagram:

Potential energy was discussed in Chapter 6.

The energy involved is potential energy that results from the attractions and repulsions among the charged particles.

The zero point of energy is defined with the atoms at infinite separation.

At very short distances the energy rises steeply because of the importance of the repulsive forces when the atoms are very close together.

The bond length is the distance at which the system has minimum energy.

In the H_2 molecule the electrons reside primarily in the space between the two nuclei where they are attracted simultaneously by both protons. This positioning is precisely what leads to the stability of the H_2 molecule compared to two separated hydrogen atoms. The potential energy of each electron is lowered because of the increased attractive forces in this area. When we say that a bond is formed between the hydrogen atoms, we mean that the H_2 molecule is more stable than two separated hydrogen atoms by a certain quantity of energy (the bond energy).

We can also think of a bond in terms of forces. The simultaneous attraction of each electron by the two protons generates a force that pulls the protons toward each other and that just balances the proton-proton and electron-electron repulsive forces at the distance corresponding to the bond length.

The type of bonding we encounter in the hydrogen molecule and in many other molecules where *electrons are shared by nuclei* is called **covalent bonding.**

Ionic and covalent bonds are the extreme bond types.

So far we have considered two extreme types of bonding. In ionic bonding the participating atoms are so different that one or more electrons are transferred to form oppositely charged ions. The bonding results from electrostatic interactions. In covalent bonding two identical atoms share electrons equally. The bonding results from the mutual attraction of the two nuclei for the shared electrons. Between these extremes are intermediate cases in which the atoms are not so different that electrons are completely transferred but are different enough so that unequal sharing results, forming what is called a **polar covalent bond.** An example of this type of bond occurs in the hydrogen fluoride (HF) molecule. When a sample of hydrogen fluoride gas is placed in an electric field, the molecules tend to orient themselves as shown in Fig. 8.2, with the fluoride end closest to the positive pole and the hydrogen end closest to the negative pole. This result implies that the HF molecule has the following charge distribution:

$$\underset{\delta+}{\text{H}}\text{—}\underset{\delta-}{\text{F}}$$

where δ (delta) is used to indicate a fractional charge. This same effect was noted in Chapter 4 where many of water's unusual properties were attributed to the polar O—H bonds in the H_2O molecule.

The most logical explanation for the development of the partial positive and negative charges on the atoms (bond polarity) in such molecules as HF and H_2O is that the electrons in the bonds are not shared equally. For example, we can account for the polarity of the HF molecule by assuming that the fluorine atom has a stronger attraction for the shared electrons than the hydrogen atom. Likewise, in the H_2O molecule the oxygen atom appears to attract the shared electrons more strongly than the hydrogen atoms do. Because bond polarity has important chemical implications, we find it useful to quantify the ability of an atom to attract shared electrons. In the next section we show how this is done.

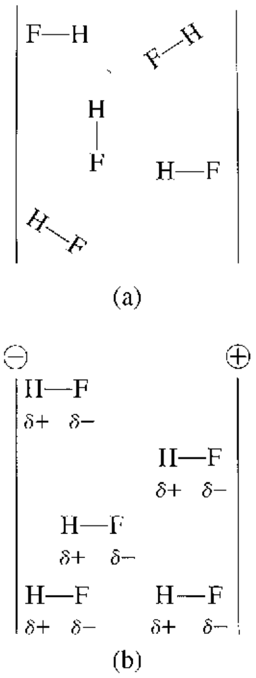


Figure 8.2

The effect of an electric field on hydrogen fluoride molecules. (a) When no electric field is present the molecules are randomly oriented. When the field is turned on (b) the molecules tend to line up with their negative ends toward the positive pole and their positive ends toward the negative pole.

8.2 Electronegativity

PURPOSE

☐ To discuss the nature of bonds in terms of electronegativity.

The different affinities of atoms for the electrons in a bond are described by a property called **electronegativity:** *the ability of an atom in a molecule to attract shared electrons to itself.*

The most widely accepted method for determining values of electronegativity is that of Linus Pauling, an American scientist who has won the Nobel Prizes for both chemistry and peace. To understand Pauling's model, consider a hypothetical molecule HX. The relative electronegativities of the H and X atoms are determined by comparing the measured H—X bond energy and the "expected" H—X bond energy, which is an average of the H—H and X—X bond energies:

$$\text{Expected H—X bond energy} = \frac{\text{H—H bond energy} + \text{X—X bond energy}}{2}$$

The difference (Δ) between the actual (measured) and expected bond energies is

$$\Delta = (\text{H—X})_{\text{act}} - (\text{H—X})_{\text{exp}}$$

If H and X have identical electronegativities, $(\text{H—X})_{\text{act}}$ and $(\text{H—X})_{\text{exp}}$ are the same and Δ is 0. On the other hand, if X has a greater electronegativity than H, the shared electron(s) will tend to be closer to the X atom. The molecule will be polar, with the following charge distribution:

$$\underset{\delta+\ \ \delta-}{\text{H—X}}$$

Note that this bond can be viewed as having an ionic, as well as a covalent, component. The electrostatic attraction between the partially charged H and X atoms will lead to a greater bond strength. Thus $(\text{H—X})_{\text{act}}$ will be larger than $(\text{H—X})_{\text{exp}}$. The greater the difference in the electronegativities of the atoms, the greater the ionic component of the bond and the greater the value of Δ. Thus the relative electronegativities of H and X can be assigned from the Δ values.

Electronegativity values have been determined by this process for virtually all of the elements; the results are given in Fig. 8.3. Note that electronegativity generally increases going from left to right across a period and decreases going down a group for the representative elements. The range of electronegativity values is from 4.0 for fluorine to 0.79 for cesium.

The relationship between electronegativity and bond type is shown in Table 8.1. For identical atoms (an electronegativity difference of zero), the electrons in the bond are shared equally and no polarity develops. When two atoms with very different electronegativities interact, electron transfer usually occurs, to produce the ions that make up an ionic substance. Intermediate cases give polar covalent bonds with unequal electron sharing.

Increasing electronegativity →

↓ Decreasing electronegativity

						H 2.1										
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La–Lu 1.0–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac 1.1	Th 1.3	Pa 1.4	U 1.4	Np–No 1.4–1.3										

Figure 8.3

The Pauling electronegativity values. Electronegativity generally increases across a period and decreases down a group.

The Relationship Between Electronegativity and Bond Type			
Electronegativity difference in the bonding atoms	**Bond type**	**Covalent character**	**Ionic character**
Zero	Covalent	Decreases ↓	Increases ↓
|	|		
Intermediate	Polar covalent		
↓	↓		
Large	Ionic		

Table 8.1

Sample Exercise 8.1

Order the following bonds according to polarity: H—H, O—H, Cl—H, S—H, and F—H.

Solution

The polarity of the bond increases as the difference in electronegativity increases. From the electronegativity values in Fig. 8.3, the following variation in bond polarity is expected (the electronegativity value appears in parentheses below each element):

$$\begin{array}{lccccccccc}
 & \text{H—H} & < & \text{S—H} & < & \text{Cl—H} & < & \text{O—H} & < & \text{F—H} \\
 & (2.1)\,(2.1) & & (2.5)\,(2.1) & & (3.0)\,(2.1) & & (3.5)\,(2.1) & & (4.0)\,(2.1) \\
\text{Electronegativity} & & & & & & & & & \\
\text{difference} & 0 & & 0.4 & & 0.9 & & 1.4 & & 1.9
\end{array}$$

$$\text{Covalent bond} \xrightarrow[\text{Polarity increases}]{} \text{Polar covalent bond}$$

8.3 Bond Polarity and Dipole Moments

PURPOSE

☐ To define the relationship between bond polarity and molecular polarity.

We have seen that when hydrogen fluoride is placed in an electric field, the molecules have a preferential orientation (Fig. 8.2). This follows from the charge distribution in the HF molecule, which has a positive end and a negative end. A molecule like HF that has a center of positive charge and a center of negative charge is said to be *dipolar,* or to have a **dipole moment.** The dipolar character of a molecule is often represented by an arrow pointing to the negative charge center with the tail of the arrow indicating the positive center of charge:

$$\begin{array}{c} +\!\!\!\longrightarrow \\ \delta+ \quad \delta- \end{array}$$

Of course, any diatomic (two-atom) molecule that has a polar bond will also show a molecular dipole moment. Polyatomic molecules can also exhibit dipolar behavior. For example, because the oxygen atom in the water molecule has a greater electronegativity than the hydrogen atoms, the molecular charge distribution is that shown in Fig. 8.4(a). Because of this charge distribution, the water molecule behaves in an electric field as if it had two centers of charge—one positive and one negative—as shown in Fig. 8.4(b). The water molecule has a dipole moment. The same type of behavior is observed for the NH_3 molecule (Fig. 8.5). Some molecules have polar bonds but do not have a dipole moment. This occurs when the individual bond polarities are arranged in such a way that they cancel each other out. An example is the CO_2 molecule, which is a linear molecule and has the charge distribution shown in Fig. 8.6. In this case, the opposing bond polarities cancel out and the carbon dioxide molecule does not have a dipole moment. There is no preferential way for this molecule to line up in an electric field. (Try to find a preferred orientation to make sure you understand this concept.)

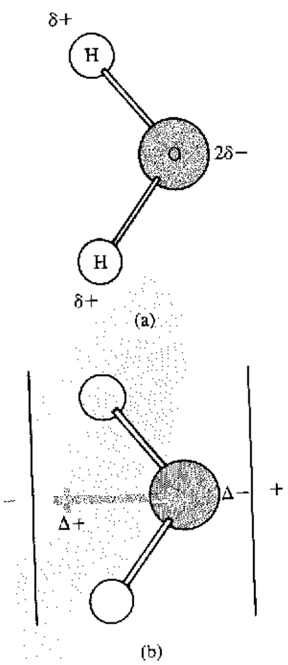


Figure 8.4

(a) The charge distribution in the water molecule. (b) The water molecule in an electric field.

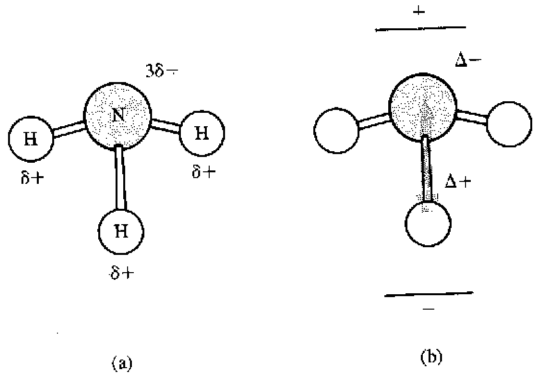


Figure 8.5

(a) The structure and charge distribution of the ammonia molecule. The polarity of the N—H bonds occurs because nitrogen has a greater electronegativity than hydrogen. (b) The dipole moment of the ammonia molecule oriented in an electric field.

The presence of polar bonds does not always yield a polar molecule.

There are many cases besides that of carbon dioxide where the bond polarities oppose and exactly cancel each other. Some common types of molecules with polar bonds but no dipole moment are shown in Table 8.2.

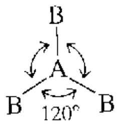
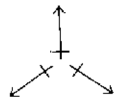
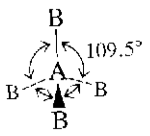
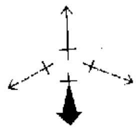
Types of Molecules with Polar Bonds but No Resulting Dipole Moment			
Type		Example	Cancellation of polar bonds
Linear molecules with two identical bonds	B—A—B	CO_2	⟵+ +⟶
Planar molecules with three identical bonds 120° apart		SO_3	
Tetrahedral molecules with four identical bonds 109.5° apart		CCl_4	

Table 8.2

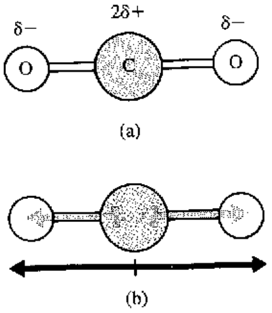


Figure 8.6

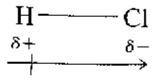
(a) The carbon dioxide molecule. (b) The opposed bond polarities cancel out, and the carbon dioxide molecule has no dipole moment.

Sample Exercise 8.2

For each of the following molecules, show the direction of the bond polarities and indicate which ones have a dipole moment: HCl, Cl_2, SO_3 (a planar molecule with the oxygen atoms spaced evenly around the central sulfur atom), CH_4 (tetrahedral (see Table 8.2) with the carbon atom at the center), and H_2S (V-shaped with the sulfur atom at the point).

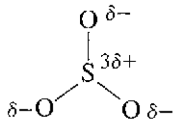
Solution

The HCl molecule: From Fig. 8.3 we can see that the electronegativity of chlorine (3.0) is greater than that of hydrogen (2.1). Thus the chlorine will be partially negative, and the hydrogen will be partially positive. The HCl molecule has a dipole moment:



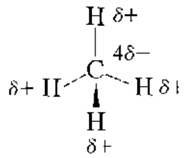
The Cl_2 molecule: The two chlorine atoms share the electrons equally. No bond polarity occurs, and the Cl_2 molecule has no dipole moment.

The SO_3 molecule: The electronegativity of oxygen (3.5) is greater than that of sulfur (2.5). This means that each oxygen will have a partial negative charge, and the sulfur will have a partial positive charge:



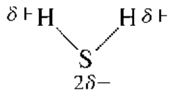
The bond polarities arranged symmetrically as shown cancel, and the molecule has no dipole moment. This molecule is the second type shown in Table 8.2.

The CH_4 molecule: Carbon has a slightly higher electronegativity (2.5) than does hydrogen (2.1). This leads to small partial positive charges on the hydrogen atoms and a small partial negative charge on the carbon:

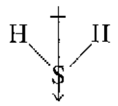


This case is similar to the third type in Table 8.2, and the bond polarities cancel. The molecule has no dipole moment.

The H_2S molecule: Since the electronegativity of sulfur (2.5) is greater than that of hydrogen (2.1), the sulfur will have a partial negative charge and the hydrogen atoms will have a partial positive charge, which can be represented as follows:



This case is analogous to the water molecule, and the polar bonds result in a dipole moment oriented as shown:



8.4 Ions: Electron Configurations and Sizes

PURPOSE

☐ To show how to predict the formulas of ionic compounds.

☐ To discuss the factors governing ion size.

Atoms in stable compounds usually have a noble gas electron configuration.

The description of the arrangements of electrons in atoms that emerged from the wave mechanical model has helped a great deal in our understanding of what constitutes a stable compound. In virtually every case the atoms in a stable compound have a noble gas arrangement of electrons. Nonmetallic elements achieve a noble gas electron configuration either by sharing electrons with other nonmetals to form covalent bonds or by taking electrons from metals to form ions. In the second case the nonmetals form anions and the metals form cations. The generalizations that apply to electron configurations in stable compounds are as follows:

▨ When *two nonmetals* react to form a covalent bond, they share electrons in a way that completes the valence electron configurations of both atoms. That is, both nonmetals attain noble gas electron configurations.

▨ When *a nonmetal and a representative group metal* react to form a binary ionic compound, the ions form so that the valence electron configuration of the nonmetal is completed and the valence orbitals of the metal are emptied. In this way both ions achieve noble gas electron configurations.

With a few exceptions these generalizations apply to the vast majority of compounds and are important to remember. We will deal with covalent bonds more thoroughly later. Next we will consider what implications these rules hold for ionic compounds.

Predicting Formulas of Ionic Compounds

To illustrate the principles of electron configurations in stable compounds, we will consider the formation of an ionic compound from calcium and oxygen. We can predict what compound will form by considering the valence electron configurations of the two atoms.

$$\mathrm{Ca:}\quad [\mathrm{Ar}]4s^2$$
$$\mathrm{O:}\quad [\mathrm{He}]2s^22p^4$$

From Fig. 8.3 we see that the electronegativity of oxygen (3.5) is much greater than that of calcium (1.0). Because of this large difference, electrons will be transferred from calcium to oxygen to form an oxygen anion and a calcium cation. How many electrons are transferred? We can base our prediction on the observation that noble gas configurations are the most stable. Note that oxygen needs two electrons to fill its $2s$ and $2p$ valence orbitals and achieve the configuration of neon ($1s^22s^22p^6$). And by losing two electrons, calcium can achieve the configuration of argon. Two electrons will therefore be transferred as shown:

$$\underbrace{\mathrm{Ca} + \mathrm{O}}_{2e^-} \rightarrow \mathrm{Ca}^{2+} + \mathrm{O}^{2-}$$

To predict the formula of the ionic compound, we must recognize that chemical compounds are always electrically neutral—they have the same quantities of positive and negative charges. In this case we must have equal numbers of Ca^{2+} and O^{2-} ions, and the empirical formula of the compound is CaO.

The same principles can be applied to many other cases. For example, consider the compound formed from aluminum and oxygen. Aluminum has the configuration [Ne]$3s^23p^1$. To achieve the neon configuration, aluminum must lose three electrons to form the Al^{3+} ion. Thus the ions will be Al^{3+} and O^{2-}. Since the compound must be electrically neutral, there must be three O^{2-} ions for every two Al^{3+} ions, and the compound has the empirical formula Al$_2$O$_3$.

Table 8.3 shows common elements that form ions with noble gas electron configurations in ionic compounds. In losing electrons to form cations, metals in Group 1A lose one electron, those in Group 2A lose two electrons, and those in Group 3A lose three electrons. In gaining electrons to form anions, nonmetals in Group 7A (the halogens) gain one electron and those in Group 6A gain two electrons. Hydrogen typically behaves as a nonmetal and can gain one electron to form the hydride ion (H$^-$), which has the electron configuration of helium.

Common Ions With Noble Gas Configurations in Ionic Compounds

Group 1A	Group 2A	Group 3A	Group 6A	Group 7A	Electron configuration
H$^-$, Li$^+$	Be^{2+}				[He]
Na$^+$	Mg^{2+}	Al^{3+}	O^{2-}	F$^-$	[Ne]
K$^+$	Ca^{2+}		S^{2-}	Cl$^-$	[Ar]
Rb$^+$	Sr^{2+}		Se^{2-}	Br$^-$	[Kr]
Cs$^+$	Ba^{2+}		Te^{2-}	I$^-$	[Xe]

Table 8.3

There are some important exceptions to the rules we have been following here. For example, tin forms both Sn^{2+} and Sn^{4+} ions, and lead forms both Pb^{2+} and Pb^{4+} ions. Bismuth forms Bi^{3+} and Bi^{5+} ions, and thallium forms Tl$^+$ and Tl^{3+} ions. There are no simple explanations for the behavior of these ions. For now, just note them as exceptions to the very useful rule that ions generally adopt noble gas electron configurations in ionic compounds. Our discussion here refers to representative metals. The transition metals exhibit more complicated behavior, forming a variety of ions that will be considered in Chapter 20.

Sizes of Ions

Ion size plays an important role in determining the structure and stability of ionic solids, the properties of ions in aqueous solution, and the biological effects of ions. Various factors influence ionic size. We will first consider the relative sizes of an ion and its parent atom. Since a positive ion is formed by taking electrons from a neutral atom, the resulting cation is smaller than its parent atom. The opposite is true for negative ions; the addition of electrons to a neutral atom produces an anion significantly larger than its parent atom. Selected examples of this behavior are shown in Fig. 8.7.

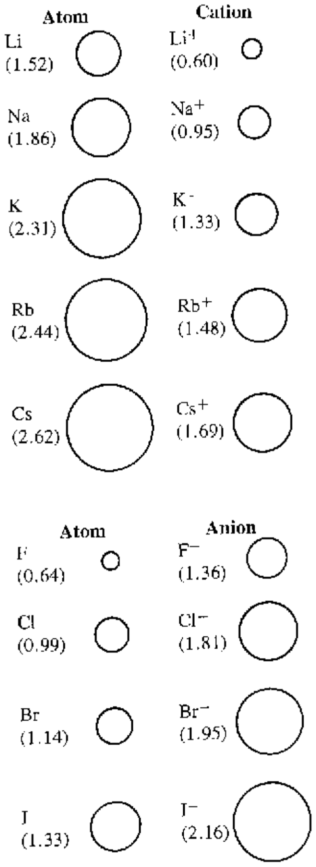


Figure 8.7

Sizes of some ions and their parent atoms. Note that cations are smaller and anions are larger than their parent atoms. The numbers in parentheses are the ionic radii given in angstroms.

Ion size increases going down a group.

It is also important to know how the sizes of ions vary depending on the positions of the elements in the periodic table. Figure 8.8 shows the sizes of the most important ions (each with a noble gas configuration) related to their position in the periodic table. Note that ion size increases going down a group. The changes that occur horizontally are complicated because there is a change from predominantly metals on the left-hand side of the periodic table to nonmetals on the right-hand side. A given period thus contains both elements that give up valence electrons to form cations and ones that accept electrons to form anions.

One trend worth noting involves the relative sizes of a set of **isoelectronic ions**—*ions containing the same number of electrons*. Consider the ions O^{2-}, F^-, Na^+, Mg^{2+}, and Al^{3+}. Each of these ions has the neon electron configuration (confirm this for yourself). How do the sizes of these ions vary? In general, there are two important facts to consider in predicting the relative sizes of ions: the number of electrons and the number of protons. Since the ions being considered here are isoelectronic, the number of electrons is ten in each case. Electron repulsions should therefore be about the same in all cases. However, the number of protons increases from eight to thirteen as we go from the O^{2-} ion to the Al^{3+} ion. Thus, in going from O^{2-} to Al^{3+}, the ten electrons experience increasing attraction by the increasing positive charge of the nucleus, which causes the ions to become smaller. You can confirm this by looking at the sizes of these ions as shown in Fig. 8.8. In general, for a series of isoelectronic ions, the size decreases as the nuclear charge (Z) increases.

For isoelectronic ions, size decreases as Z increases.

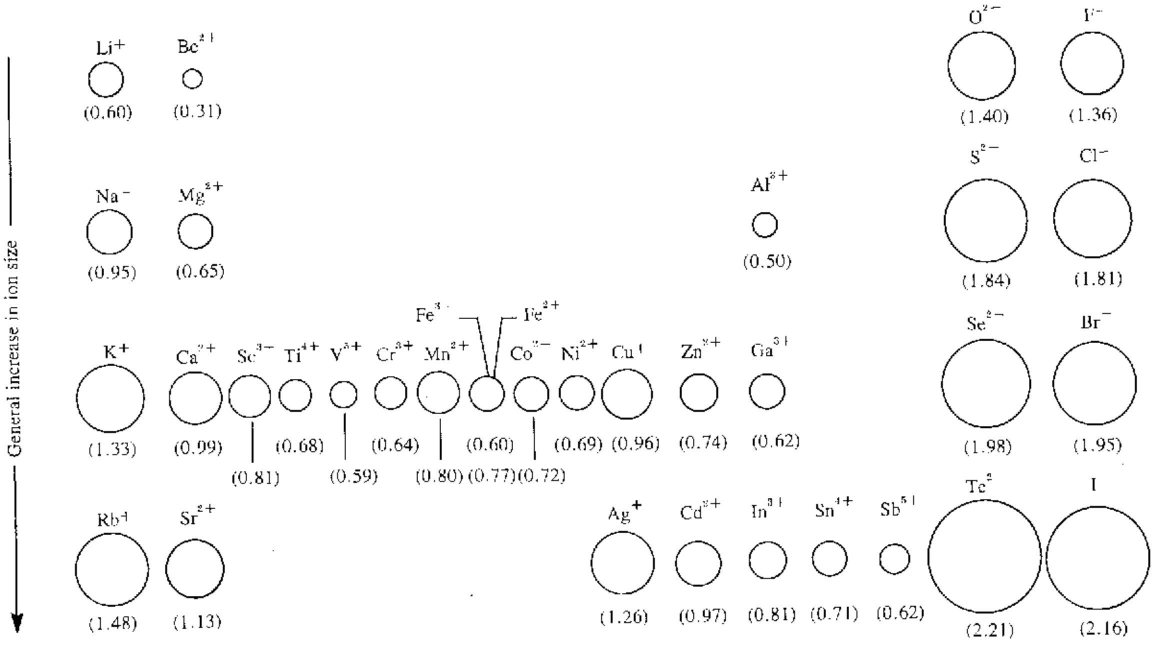


Figure 8.8

Sizes of ions related to positions of elements in the periodic table. Note that size generally increases going down a group. Also note that in a series of isoelectronic ions size decreases with increasing atomic number. The numbers in parentheses are the ionic radii in units of angstroms.

Sample Exercise 8.3

Arrange the ions Se^{2-}, Br^-, Rb^+, and Sr^{2+} in order of decreasing size.

Solution

This is an isoelectronic series of ions with the electron configuration of krypton. Since these ions all have the same number of electrons, their sizes will depend on nuclear charge (Z). The Z values are 34 for Se^{2-}, 35 for Br^-, 37 for Rb^+, and 38 for Sr^{2+}. Since the nuclear charge is greatest for the Sr^{2+} ion, it will be the smallest of these ions. The Se^{2-} ion with the smallest value of Z will be the largest:

$$\underset{\substack{\uparrow\\ \text{Largest}}}{Se^{2-}} > Br^- > Rb^+ > \underset{\substack{\uparrow\\ \text{Smallest}}}{Sr^{2+}}$$

Sample Exercise 8.4

Choose the largest ion in each of the following groups:

a. Li^+, Na^+, K^+, Rb^+, Cs^+ **b.** Ba^{2+}, Cs^+, I^-, Te^{2-}

Solution

a. The ions are all from Group 1A elements. Since size increases going down a group (the ion with the greatest number of electrons is the largest), Cs^+ is the largest ion.

b. This is an isoelectronic series of ions, all of which have the electron configuration of xenon. The ion with the smallest nuclear charge will be the largest ion:

$$\underset{Z=52}{Te^{2-}} > \underset{Z=53}{I^-} > \underset{Z=55}{Cs^+} > \underset{Z=56}{Ba^{2+}}$$

8.5 Binary Ionic Compounds

PURPOSE

☐ To define lattice energy and to show how it can be calculated.

In this section we will introduce the factors influencing the formation and structures of binary ionic compounds. We know that metals and nonmetals react by transferring electrons to form cations and anions that are mutually attractive. The resulting ionic solid forms because the aggregated oppositely charged ions have lower energy than the original elements. Just how strongly the ions attract each other in the solid state is indicated by the **lattice energy**—*the change in energy that takes place when separated gaseous ions are packed together to form an ionic solid:*

$$M^+(g) + X^-(g) \rightarrow MX(s)$$

The lattice energy is often defined as the energy *released* when an ionic solid forms from its ions. However, in this book, the sign of the lattice energy will be determined from the system's point of view: negative if the process is exothermic; positive if endothermic.

The structures of ionic solids will be discussed in detail in Chapter 10

We can illustrate the energy changes involved in the formation of an ionic solid by considering the formation of solid lithium fluoride from its elements:

$$Li(s) + \tfrac{1}{2}F_2(g) \rightarrow LiF(s)$$

To see the energy terms associated with this process, we will take advantage of the fact that energy is a state function and break this reaction down into steps, the sum of which gives the overall reaction:

STEP 1
Sublimation of solid lithium. Sublimation involves taking a substance from the solid state to the gaseous state:

$$\mathrm{Li}(s) \rightarrow \mathrm{Li}(g)$$

The energy of sublimation for Li(s) is 161 kJ/mol.

STEP 2
Ionization of lithium atoms to form Li^+ ions in the gas phase:

$$\mathrm{Li}(g) \rightarrow \mathrm{Li}^+(g) + e^-$$

This process corresponds to the first ionization energy for lithium, which is 520 kJ/mol.

STEP 3
Dissociation of fluorine molecules. We need to form 1 mole of fluorine atoms by breaking the F—F bond in $\frac{1}{2}$ mole of F_2 molecules:

$$\frac{1}{2}\,\mathrm{F}_2(g) \rightarrow \mathrm{F}(g)$$

The energy required to break this bond is known from experiment to be 154 kJ/mol. In this case we are breaking the bonds in a half mole of fluorine, so the energy required for this step is 154 kJ/2, or 77 kJ.

STEP 4
Formation of F^- ions from fluorine atoms in the gas phase:

$$\mathrm{F}(g) + e^- \rightarrow \mathrm{F}^-(g)$$

We have defined the energy change for this process as the electron affinity of fluorine, which is −328 kJ/mol.

STEP 5
Formation of solid lithium fluoride from the gaseous Li^+ and F^- ions:

$$\mathrm{Li}^+(g) + \mathrm{F}^-(g) \rightarrow \mathrm{LiF}(s)$$

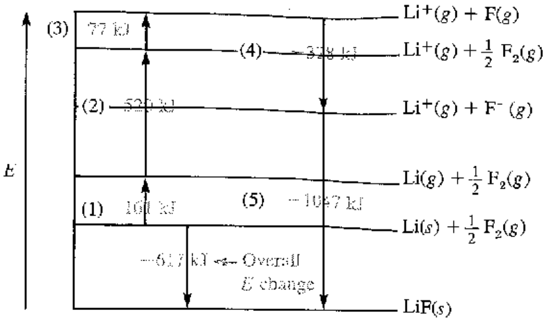
This corresponds to the definition of the lattice energy for LiF, which is known to be −1047 kJ/mol.

Since the sum of these five processes gives the overall reaction desired, the sum of the individual energy changes gives the overall energy change:

	Process	Energy change (kJ)
	$\mathrm{Li}(s) \rightarrow \mathrm{Li}(g)$	161
	$\mathrm{Li}(g) \rightarrow \mathrm{Li}^+(g) + e^-$	520
	$\frac{1}{2}\mathrm{F}_2(g) \rightarrow \mathrm{F}(g)$	77
	$\mathrm{F}(g) + e^- \rightarrow \mathrm{F}^-(g)$	−328
	$\mathrm{Li}^+(g) + \mathrm{F}^-(g) \rightarrow \mathrm{LiF}(s)$	−1047
Overall:	$\mathrm{Li}(s) + \frac{1}{2}\mathrm{F}_2(g) \rightarrow \mathrm{LiF}(s)$	−617 kJ (per mole of LiF)

Figure 8.9

The energy changes involved in the formation of solid lithium fluoride from its elements. Step (1) represents sublimation of solid lithium. Step (2) represents the ionization of lithium atoms in the gas phase. Step (3) represents dissociation of a half mole of gaseous fluorine molecules. Step (4) represents the addition of electrons to fluorine atoms in the gas phase. Step (5) represents formation of solid lithium fluoride from the gaseous ions.



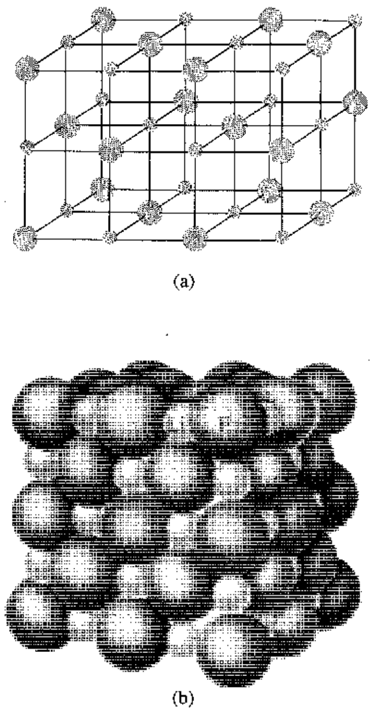
This process is summarized by the energy diagram in Fig. 8.9. Note that the formation of solid lithium flouride from its elements is highly exothermic, mainly because of the very large negative lattice energy. A great deal of energy is released when the ions combine to form the solid. In fact, note that the energy released when an electron is added to a fluorine atom to form the F^- ion (328 kJ/mol) is not enough to remove an electron from lithium (520 kJ/mol). That is, when a metallic lithium atom reacts with a nonmetallic fluorine atom to form *separated* ions,

$$Li(g) + F(g) \rightarrow Li^+(g) + F^-(g)$$

the process is endothermic and thus unfavorable. Clearly then, the main impetus for the formation of an ionic compound rather than a covalent compound in this case results from the strong mutual attractions of the Li^+ and F^- ions in the solid. The lattice energy is the dominant energy term.

The structure of the solid lithium fluoride is represented in Fig. 8.10. Note the alternating arrangement of the Li^+ and F^- ions, and that each Li^+ is surrounded by six F^- ions and each F^- ion is surrounded by six Li^+ ions. This structure can be rationalized by assuming that the ions behave as hard spheres that pack in a way that both maximizes the attractions among the oppositely charged ions and minimizes the repulsions among the identically charged ions.

All of the binary ionic compounds formed by an alkali metal and a halogen have the structure shown in Fig. 8.10, except the cesium salts. The arrangement of ions shown in Fig. 8.10 is often called the *sodium chloride structure* after the most common substance that possesses it.


(a)

(b)

Figure 8.10

The structure of lithium fluoride. (a) Represented by a ball and stick model. Note that each Li^+ ion is surrounded by six F^- ions, and each F^- ion is surrounded by six Li^+ ions. (b) Represented with the ions shown as spheres. The structure is determined by packing the spherical ions in a way that both maximizes the ionic attractions and minimizes the ionic repulsions.

Lattice Energy Calculations

In the discussion of the energetics of the formation of solid lithium fluoride, we emphasized the importance of lattice energy in contributing to the stability of ionic solids. Lattice energy can be represented by Coulomb's law,

$$\text{Lattice energy} = k\left(\frac{Q_1Q_2}{r}\right)$$

where k is a proportionality constant that depends on the structure of the solid and the electron configurations of the ions, Q_1 and Q_2 are the charges on the ions, and r is the shortest distance between the centers of the cations and anions. Note that the lattice energy has a negative sign when Q_1 and Q_2 have opposite signs. This is to be expected, since bringing cations and anions together is an exothermic process. Also note that the process becomes more exothermic as the ionic charges increase and the distances between the ions in the solid decrease.

The importance of charge in ionic solids can be illustrated by comparing the energies involved in the formation of NaF(*s*) and MgO(*s*) where the ions involved, Na^+, F^-, Mg^{2+}, and O^{2-}, are isoelectronic. The energy diagram for the formation of the two ionic solids is given in Fig. 8.11. There are several important features to note:

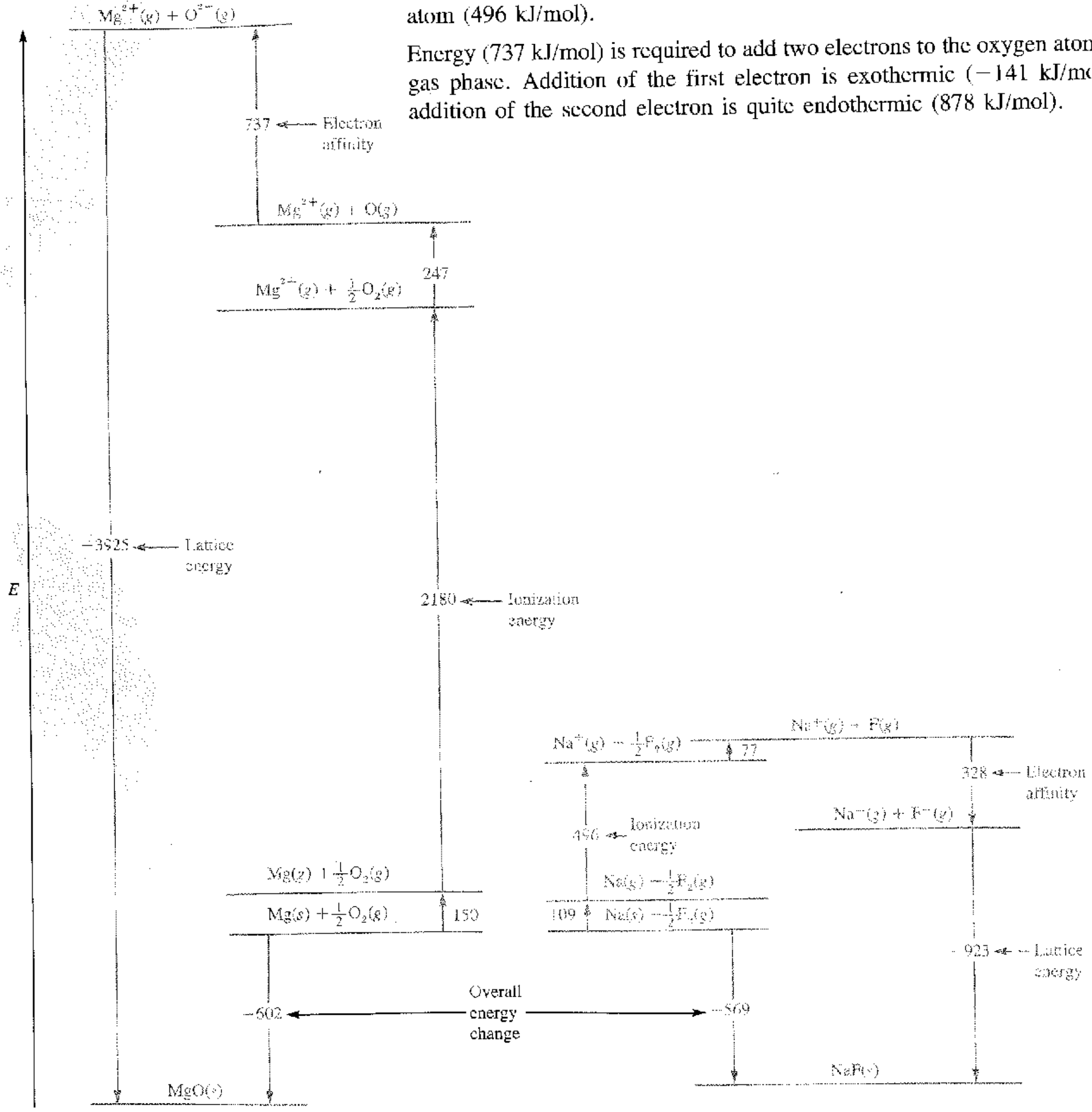
The energy released when gaseous Mg^{2+} and O^{2-} ions combine to form MgO(s) is much greater than that released when gaseous Na^+ and F^- ions combine to form NaF(*s*).

The energy required to remove two electrons from the magnesium atom (735 kJ/mol for the first and 1445 kJ/mol for the second for a total of 2180 kJ/mol) is much greater than the energy required to remove an electron from a sodium atom (496 kJ/mol).

Energy (737 kJ/mol) is required to add two electrons to the oxygen atom in the gas phase. Addition of the first electron is exothermic (−141 kJ/mol), but addition of the second electron is quite endothermic (878 kJ/mol).

Figure 8.11

Comparison of the energy changes involved in the formation of solid sodium fluoride and solid magnesium oxide. Note the large lattice energy for magnesium oxide (where doubly charged ions are combining) compared to that for sodium fluoride (where singly charged ions are combining).



In view of the facts that twice as much energy is required to remove the second electron from magnesium as to remove the first and that addition of an electron to the gaseous O^- ion is quite endothermic, it seems puzzling that magnesium oxide contains Mg^{2+} and O^{2-} ions rather than Mg^+ and O^- ions. The answer to this lies in the lattice energy. Note that the lattice energy for combining gaseous Mg^{2+} and O^{2-} ions to form $MgO(s)$ is 3000 kJ/mol more negative than that for combining gaseous Na^+ and F^- ions to form $NaF(s)$. Thus the energy released in forming a solid containing Mg^{2+} and O^{2-} ions rather than Mg^+ and O^- ions more than compensates for the energies required for the processes that produce the Mg^{2+} and O^{2-} ions.

If there is so much lattice energy to be gained in going from singly charged to doubly charged ions in the case of magnesium oxide, why then does solid sodium fluoride contain Na^+ and F^- ions rather than Na^{2+} and F^{2-} ions? We can answer this question by recognizing that both Na^+ and F^- ions have the neon electron configuration. Removal of an electron from Na^+ would require an extremely large quantity of energy, since it would be a 2*p* electron. Conversely, the addition of an electron to F^- would require use of the relatively large 3*s* orbital, which is also an unfavorable process. We can say that for sodium fluoride the extra energy required to form the doubly charged ions is greater than the gains in lattice energy that would result.

This comparison of the energies involved in the formation of sodium fluoride and magnesium oxide illustrates that a variety of factors operates to determine the composition and structure of ionic compounds. The most important of these factors involve the balancing of the energies required to form highly charged ions and the energy released when highly charged ions combine to form the solid.

8.6 Partial Ionic Character of Covalent Bonds

PURPOSE

☐ To show the relationship between electronegativity and the ionic character of a bond.

When atoms with different electronegativities react to form compounds, the electrons are not shared equally. The possible result is a polar covalent bond or, in the case of a large electronegativity difference, a complete transfer of one or more electrons to form ions. The cases are summarized in Fig. 8.12.

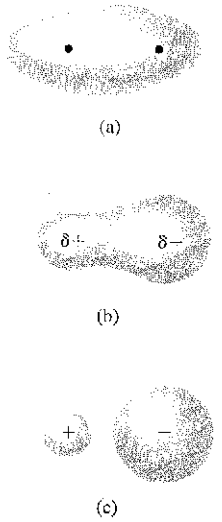


Figure 8.12

The three possible types of bonds: (a) a covalent bond formed between identical atoms; (b) a polar covalent bond, with both ionic and covalent components; and (c) an ionic bond, with no electron sharing.

How well can we tell the difference between an ionic bond and a polar covalent bond? The only honest answer to this question is that there are probably no totally ionic bonds. The evidence for this statement comes from calculations of the percent ionic character in various binary compounds. These calculations are based on comparisons of the measured dipole moments for molecules of the type X—Y with the calculated dipole moments for the completely ionic case, X^+Y^-. The percent ionic character of a bond is then defined as follows:

$$\text{Percent ionic character of a bond} = \left(\frac{\text{measured dipole moment of X—Y}}{\text{calculated dipole moment of } X^+Y^-}\right) \times 100$$

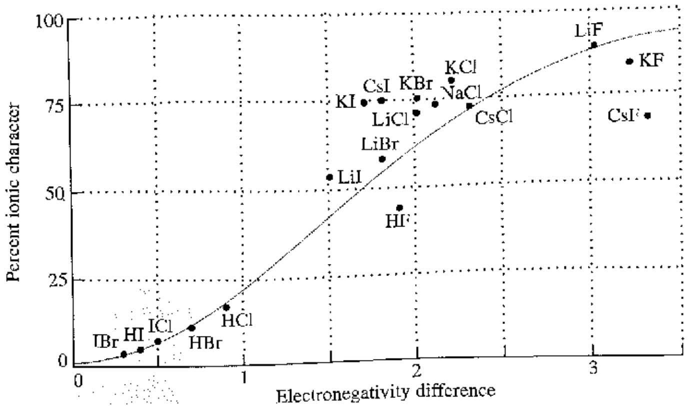


Figure 8.13

The relationship between the ionic character of a covalent bond and the electronegativity difference of the bonded atoms.

Application of this definition to various ionic compounds gives the results shown in Fig. 8.13, where percent ionic character is plotted versus the difference in the electronegativity values of X and Y. Note from this plot that ionic character increases with electronegativity difference, as expected. However, none of the compounds reaches 100% ionic character, even though compounds with the maximum possible electronegativity differences are considered. Thus, according to this definition, no compounds are completely ionic. This is in contrast to the usual classification of these compounds. All of the compounds shown in Fig. 8.13 with more than 50% ionic character are normally considered to be ionic.

Another complication in identifying ionic compounds is that many substances contain polyatomic ions. For example, NH_4Cl contains NH_4^- and Cl^- ions, and Na_2SO_4 contains Na^+ and SO_4^{2-} ions. The ammonium and sulfate ions are held together by covalent bonds. Thus calling NH_4Cl and Na_2SO_4 ionic compounds is somewhat ambiguous.

We will avoid these problems by adopting an operational definition of ionic compounds: *any solid that conducts an electric current when melted or dissolved in water will be classified as ionic.* Also, the generic term *salt* will be used interchangeably with *ionic compound* in this book.

8.7 The Covalent Chemical Bond—A Model

PURPOSE

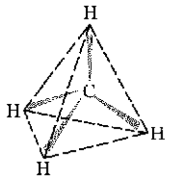
☐ To discuss the covalent bonding model.

Before we develop specific models of covalent chemical bonding, it will be helpful if we summarize some of the concepts that have been introduced in this chapter.

What is a chemical bond? A chemical bond can be viewed as a force that causes a group of atoms to behave as a unit.

Why do chemical bonds occur? There is no principle of nature that states that bonds are favored or disfavored. Bonds are neither inherently "good" nor inherently "bad" as far as nature is concerned, but they result from the tendency of a system to seek its lowest possible energy. From a simplistic point of view, bonds occur where collections of atoms are more stable (lower in energy) than are the separate atoms. For example, approximately 1652 kJ of energy is required to break a mole of methane (CH_4) molecules into separate C and H atoms. Or, to take the opposite view, 1652 kJ of energy is released when 1 mole of methane is formed from 1 mole of gaseous C atoms and 4 moles of gaseous H atoms. Thus we can say that 1 mole of CH_4 molecules in the gas phase is 1652 kJ lower in energy than 1 mole of carbon atoms plus 4 moles of hydrogen atoms. Methane is therefore a stable molecule relative to the separated atoms.

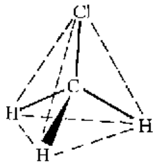
We find it useful to interpret molecular stability in terms of a model called a *chemical bond*. To understand why this model has been invented, let's continue with methane, which consists of four hydrogen atoms arranged around a carbon atom at the corners of a tetrahedron:



Given this structure, it is natural to envision four individual C—H interactions (we call them bonds). The energy of stabilization of CH_4 is divided equally among them to give an average C—H bond energy per mole of C—H bonds:

$$\frac{1652\ \text{kJ}}{4} = 413\ \text{kJ}$$

Next consider methyl chloride, which consists of CH_3Cl molecules having the structure



From experiment, it has been determined that approximately 1578 kJ of energy is required to break down 1 mole of gaseous CH_3Cl molecules into gaseous carbon, chlorine, and hydrogen atoms. The reverse process can be represented as:

$$C(g) + Cl(g) + 3H(g) \rightarrow CH_3Cl + 1578\ \text{kJ/mol}$$

A mole of gaseous methyl chloride is lower in energy by 1578 kJ than its separate gaseous atoms. Thus a mole of methyl chloride is held together by 1578 kJ of energy. Again, it is very useful to divide this energy into individual bonds. Methyl chloride can be visualized as containing one C—Cl bond and three C—H bonds. If we assume arbitrarily that a C—H interaction represents the same quantity of energy in any situation (that is, that the strength of a C—H bond is independent of its molecular environment), we can do the following bookkeeping:

$$\begin{aligned}
1\ \text{mol of C—Cl bonds plus 3 mol of C—H bonds} &= 1578\ \text{kJ}\\
\text{C—Cl bond energy} + 3(\text{average C—H bond energy}) &= 1578\ \text{kJ}\\
\text{C—Cl bond energy} + 3(413\ \text{kJ/mol}) &= 1578\ \text{kJ}\\
\text{C—Cl bond energy} = 1578 - 1239 &= 339\ \text{kJ/mol}
\end{aligned}$$

These assumptions allow us to associate given quantities of energy with C—H and C—Cl bonds.

Bonding is a model proposed to explain molecular stability.

It is important to note that the bond concept is a human invention. Bonds simply provide a method for dividing up the energy evolved when a stable molecule is formed from its component atoms. A *bond thus represents a quantity of energy* obtained from the overall molecular energy in a rather arbitrary way. This is not to say that the bonding concept is a bad idea. In fact, the modern concept of the chemical bond, conceived by the American chemists G. N. Lewis and Linus Pauling, is one of the most useful ideas chemists have ever conceived.

Models—An Overview

Models were introduced in Chapter 1.

The framework of chemistry, like that of any science, consists of models—attempts to explain how nature operates on the microscopic level, based on experiences in the macroscopic world. To understand chemistry it is essential to understand its models and how they are used. We will use the concept of bonding to reemphasize the important characteristics of models including their origin, structure, and uses.

Models originate from our observations of the properties of nature. For example, the concept of bonds arose from the observations that most chemical processes involve collections of atoms and that chemical reactions involve rearrangements of the ways the atoms are grouped. So to understand reactions we must understand the forces that bind atoms together.

The reason nature seeks the lowest energy state is discussed in Chapter 16.

In natural processes there is a tendency toward lower energy. Collections of atoms therefore occur because the aggregated state has lower energy than the separated atoms. Why? As we have seen earlier in this chapter, the best explanation for the energy change involves either atoms sharing electrons or atoms transferring electrons to become ions. In the case of electron sharing, we find it convenient to assume that individual bonds occur between pairs of atoms. Let's explore the validity of this assumption and see how it is useful.

In a diatomic molecule such as H_2, it is natural to assume that a bond exists between the atoms that holds them together. It is also useful to assume that individual bonds are present in polyatomic molecules such as CH_4. So instead of thinking of CH_4 as a unit with a stabilization energy of 1652 kJ per mole, we choose to think of CH_4 as containing four C—H bonds, each worth 413 kJ of energy per mole of bonds. Without this concept of individual bonds in molecules, chemistry would be hopelessly complicated. There are millions of different chemical compounds, and if each of these compounds had to be considered as an entirely new entity, the task of understanding chemical behavior would be overwhelming.

The bonding model provides a framework to systematize chemical behavior by enabling us to think of molecules as collections of common fundamental components. For example, a typical biomolecule, such as a protein, contains hundreds of atoms and might seem discouragingly complex. However, if we think of a protein as being constructed with individual bonds: C—C, C—H, C—N, C—O, N—H, and so on, it helps tremendously in predicting and understanding the protein's behavior. The essential idea is that we expect a given bond to behave about the same in any molecular environment. Used in this way, the model of the chemical bond has helped chemists to systematize the reactions of the millions of existing compounds.

In addition to being very useful, the bonding model is also physically sensible. It makes sense that atoms can form stable groups by sharing electrons. Shared electrons give a lower energy state because they are simultaneously attracted by two nuclei.

Also, as we will see in the next section, bond energy data support the existence of discrete bonds that are relatively independent of the molecular environment. It is very important to remember, however, that the chemical bond is only a model. While our concept of discrete bonds in molecules agrees with many of our observations, some molecular properties require that we think of a molecule as a whole, with the electrons free to move through the entire molecule. This is called *delocalization* of the electrons, a concept that will be discussed more completely in the next section.

It is essential that anyone who studies science understand the construction and the use of models. They have several fundamental properties:

Understand both the power and limitations of chemical models.

1. Models are human inventions, always based on an incomplete understanding of how nature works. *A model does not equal reality.*
2. Models are often wrong. This property derives from the first property. Models are based on speculation and are always oversimplifications.
3. Models tend to become more complicated as they age. As flaws are discovered in our models, we patch them by adding more assumptions.
4. It is very important to understand the assumptions inherent in a particular model before you use it to interpret observations or to make predictions. Simple models usually involve very restrictive assumptions and can only be expected to yield qualitative information. Asking for a sophisticated explanation from a simple model is like expecting to get an accurate mass for a diamond using a bathroom scale.

   If a model is to be used effectively, we must understand its strengths and weaknesses and ask only appropriate questions. An illustration of this point is the simple Aufbau principle used to explain the electron configurations of the elements. Although this model correctly predicts the configuration for most atoms, chromium and copper do not agree with the predictions. Detailed studies show that the configurations of chromium and copper result from complex electron interactions that are not taken into account in the model. But this does not mean that we should discard the simple model that is so useful for most atoms. Instead, we should apply it with caution and not expect it to be correct in every case.
5. When a model is wrong, we often learn much more than when it is right. If a model makes a wrong prediction, it usually means we do not understand some fundamental characteristics of nature. We often learn by making mistakes (try to remember that when you get back your next chemistry test).

8.8

Covalent Bond Energies and Chemical Reactions

PURPOSE

☐ To describe the relationship of bond energy to bond multiplicity.

☐ To show how bond energies can be used to calculate heats of reaction.

In this section we will consider the energies associated with various types of bonds and see how the bonding concept is useful in dealing with the energies of chemical reactions. One important consideration is to establish the sensitivity of a particular type of bond to its molecular environment. For example, consider the stepwise decomposition of methane shown below:

Process	Energy required (kJ/mol)
$CH_4(g) \rightarrow CH_3(g) + H(g)$	435
$CH_3(g) \rightarrow CH_2(g) + H(g)$	453
$CH_2(g) \rightarrow CH(g) + H(g)$	425
$CH(g) \rightarrow C(g) + H(g)$	339
	Total = 1652
	Average = $\frac{1652}{4}$ = 413

Although a C—H bond is being broken in each case, the energy required varies in a nonsystematic way. This shows that the C—H bond is somewhat sensitive to its environment. We use the *average* of these individual bond dissociation energies even though this quantity only approximates the energy associated with a C—H bond in a particular molecule. Similar measurements on other types of bonds have provided the values for bond energies listed in Table 8.4.

Average Bond Energies (kJ/mol)

Single bonds

H—H	432	N—H	391	I—I	149
H—F	565	N—N	160	I—Cl	208
H—Cl	427	N—F	272	I—Br	175
H—Br	363	N—Cl	200		
H—I	295	N—Br	243	S—H	347
				S—F	327
C—H	413	O—H	467	S—Cl	253
C—C	347	O—O	146	S—Br	218
C—N	305	O—F	190	S—S	266
C—O	358	O—Cl	203		
C—F	485	O—I	234	Si—Si	226
C—Cl	339			Si—H	323
C—Br	276	F—F	154	Si—C	301
C—I	240	F—Cl	253	Si—O	368
C—S	259	F—Br	237		
		Cl—Cl	239		
		Cl—Br	218		
		Br—Br	193		

Multiple bonds

C=C	614
C≡C	839
O=O	495
C=O	799
C≡O	1072
N=N	418
N≡N	941

Table 8.4

So far, we have discussed bonds where one pair of electrons is shared. This type of bond is called a **single bond.** As we will see in more detail later, atoms sometimes share two pairs of electrons, forming a **double bond,** or share three pairs of electrons, forming a **triple bond.** The bond energies for these *multiple bonds* are also given in Table 8.4.

There is also a relationship between the number of shared electron pairs and the bond length. As the number of shared electrons increases, the bond length shortens. This relationship is shown for selected bonds in Table 8.5.

Bond Lengths for Selected Bonds

Bond	Bond type	Bond length (Å)	Bond energy (kJ/mol)
C—C	single	1.54	347
C═C	double	1.37	614
C≡C	triple	1.20	839
C—O	single	1.43	358
C═O	double	1.23	799
C—N	single	1.43	305
C═N	double	1.38	615
C≡N	triple	1.16	891

Table 8.5

Bond Energy and Enthalpy

Bond energy values can be used to calculate approximate energies for reactions. To illustrate how this is done, we will calculate the change in energy that accompanies the following reaction:

$$H_2(g) + F_2(g) \rightarrow 2HF(g)$$

This reaction involves breaking one H—H and one F—F bond and forming two H—F bonds. To break bonds energy must be *added* to the system, which is an endothermic process. This means that the energy terms associated with bond breaking will have *positive* signs. The formation of a bond *releases* energy, an exothermic process, and the energy terms associated with bond making will carry a *negative* sign. We can write the enthalpy change for the reaction as follows:

ΔH = sum of the energies required to break old bonds (positive signs) plus the energies released from the formation of new bonds (negative signs)

This leads to the expression

$$\Delta H = \underbrace{\Sigma D \text{ (bonds broken)}}_{\text{Energy required}} - \underbrace{\Sigma D \text{ (bonds formed)}}_{\text{Energy released}}$$

where Σ represents the sum of terms and D represents the bond energy per mole of bonds. (D *always* has a positive sign.)

In the case of the formation of HF:

$$\Delta H = D_{\text{H—H}} + D_{\text{F—F}} - 2D_{\text{H—F}}$$

$$= 1 \text{ mol} \times \frac{432 \text{ kJ}}{\text{mol}} + 1 \text{ mol} \times \frac{154 \text{ kJ}}{\text{mol}} - 2 \text{ mol} \times \frac{565 \text{ kJ}}{\text{mol}} = -544 \text{ kJ}$$

Thus when 1 mole of $H_2(g)$ and 1 mole of $F_2(g)$ react to form 2 moles of $HF(g)$, 544 kJ of energy should be released.

Sample Exercise 8.5

Using the bond energies listed in Table 8.4, calculate ΔH for the reaction of methane with chlorine and fluorine to give Freon-12, CF_2Cl_2.

$$CH_4(g) + 2Cl_2(g) + 2F_2(g) \rightarrow CF_2Cl_2(g) + 2HF(g) + 2HCl(g)$$

Solution

The idea here is to break the bonds in the reactants to give individual atoms and then assemble these atoms into the products by forming new bonds:

$$\text{Reactants} \xrightarrow[\text{required}]{\text{Energy}} \text{atoms} \xrightarrow[\text{released}]{\text{Energy}} \text{products}$$

We then combine the energy changes to calculate ΔH:

ΔH = energy required to break bonds − energy released when bonds form

where the minus sign gives the correct sign to the energy terms for the exothermic processes.

Reactant bonds broken:

Reactants	Bonds	Energy required
CH_4	4 mol C—H	$4 \text{ mol} \times \frac{413 \text{ kJ}}{\text{mol}} = 1652 \text{ kJ}$
$2Cl_2$	2 mol Cl—Cl	$2 \text{ mol} \times \frac{239 \text{ kJ}}{\text{mol}} = 478 \text{ kJ}$
$2F_2$	2 mol F—F	$2 \text{ mol} \times \frac{154 \text{ kJ}}{\text{mol}} = 308 \text{ kJ}$
		Total energy required = 2438 kJ

Product bonds formed:

Products	Bonds	Energy released
CF_2Cl_2	2 mol C—F and	$2 \text{ mol} \times \frac{485 \text{ kJ}}{\text{mol}} = 970 \text{ kJ}$
	2 mol C—Cl	$2 \text{ mol} \times \frac{339 \text{ kJ}}{\text{mol}} = 678 \text{ kJ}$
HF	2 mol H—F	$2 \text{ mol} \times \frac{565 \text{ kJ}}{\text{mol}} = 1130 \text{ kJ}$
HCl	2 mol H—Cl	$2 \text{ mol} \times \frac{427 \text{ kJ}}{\text{mol}} = 854 \text{ kJ}$
		Total energy released = 3632 kJ

We now can calculate ΔH:

$$\begin{aligned}\Delta H &= \text{energy required to break bonds} - \text{energy released when bonds form} \\ &= 2438 \text{ kJ} - 3632 \text{ kJ} \\ &= -1194 \text{ kJ}\end{aligned}$$

Since the sign of the value for the enthalpy change is negative, this means that 1194 kJ of energy is released per mole of CF_2Cl_2 formed.

8.9 Covalent Bonding Models

PURPOSE

☐ To compare and contrast the molecular orbital model and the localized electron model.

So far we have discussed the general characteristics of the chemical bonding model and have seen that properties such as bond strength and polarity can be assigned to individual bonds. In this section we introduce two specific models used to describe covalent bonds: the molecular orbital model and the localized electron model (often called the valence bond model).

The **molecular orbital (MO) model** considers a molecule to be a collection of nuclei and electrons that can be treated using the same type of wave mechanics applied successfully to individual atoms. The fundamental idea is that the electrons occupy orbitals in the molecule in much the same way that they occupy orbitals in atoms and thus that the electron probability will extend over the entire molecule: the orbitals are **molecular orbitals** and are characterized by **delocalization** of the electrons.

The MO model has been applied to a wide range of molecules and has been quite successful in accounting for their properties. Although an excellent physical model (it seems to describe nature quite accurately), the MO model has a major disadvantage: its application to anything but very simple molecules requires rather sophisticated mathematical procedures. We need a simpler model that can be easily applied even to very complicated molecules and that can be used routinely by chemists to interpret and organize the wide variety of chemical phenomena. The model that serves this purpose is the **localized electron (LE) model,** which assumes that *a molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms.* Electron pairs in the molecule are assumed to be localized on a particular atom or in the space between two atoms. Those pairs of electrons localized on an atom are called **lone pairs,** and those found in the space between the atoms are called **bonding pairs.**

As we will apply it, the LE model has three parts:

1. Description of the valence electron arrangement in the molecule using Lewis structures, discussed in the next section.
2. Prediction of the geometry of the molecule, using the valence shell electron pair repulsion (VSEPR) model, discussed in Section 8.13.
3. Description of the types of atomic orbitals used by the atoms to share electrons or hold lone pairs. We will discuss orbitals in Chapter 9, where a more detailed description of the bonding models will be presented.

At this point, it is instructive to compare the two models. The MO model regards a molecule as a collection of nuclei and delocalized electrons, and the LE model regards a molecule as a collection of atoms with localized electron pairs. The MO model requires sophisticated mathematics but can furnish us with quantitative information such as bond strengths and bond lengths for molecules. The LE model, as we will use it, is a qualitative model that is easy to apply but gives little quantitative information. Thus the two models complement each other: one gives a detailed description of molecules while the other provides a simple means for predicting and systematizing qualitative properties of molecules. In this text we'll describe and apply the LE model extensively and give only an introduction to the MO model.

8.10 Lewis Structures

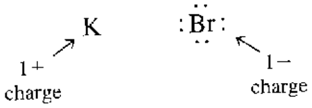
PURPOSE

☐ To show how to write Lewis structures.

The **Lewis structure** of a molecule shows how the valence electrons are arranged among the atoms in the molecule. These representations are named after G. N. Lewis (Fig. 8.14). The rules for writing Lewis structures are based on observations of thousands of molecules. From experiment, chemists have learned that the *most important requirement for the formation of a stable compound is that the atoms achieve noble gas electron configurations.*

Lewis structures show only valence electrons.

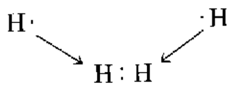
We have already seen that when metals and nonmetals react to form binary ionic compounds, electrons are transferred and the resulting ions typically have noble gas electron configurations. An example is the formation of KBr where the K^+ ion has the [Ar] electron configuration and the Br^- ion has the [Kr] electron configuration. In writing Lewis structures, the rule is that *only the valence electrons are included.* Using dots to represent electrons, the Lewis structure for KBr is



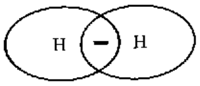
No dots are shown on the K^+ ion since it has no valence electrons. The Br^- ion is shown with eight electrons since it has a filled valence shell.

Next we will consider Lewis structures for molecules with covalent bonds, involving elements in the first and second periods. The principle of achieving a noble gas electron configuration applies to these elements as follows:

1. Hydrogen forms stable molecules where it shares two electrons. That is, it follows a **duet rule.** For example, when two hydrogen atoms, each with one electron, combine to form the H_2 molecule, we have



By sharing electrons, each hydrogen in H_2, in effect, has two electrons; that is, each hydrogen has a filled valence shell.



2. Helium does not form bonds because its valence orbitals are already filled; it is a noble gas. Helium has the electron configuration $1s^2$ and can be represented by the Lewis structure

He:

3. The second row nonmetals carbon through fluorine form stable molecules when they are surrounded by enough electrons to fill the valence orbitals, that is, the 2*s* and the three 2*p* orbitals. Since eight electrons are required to fill these

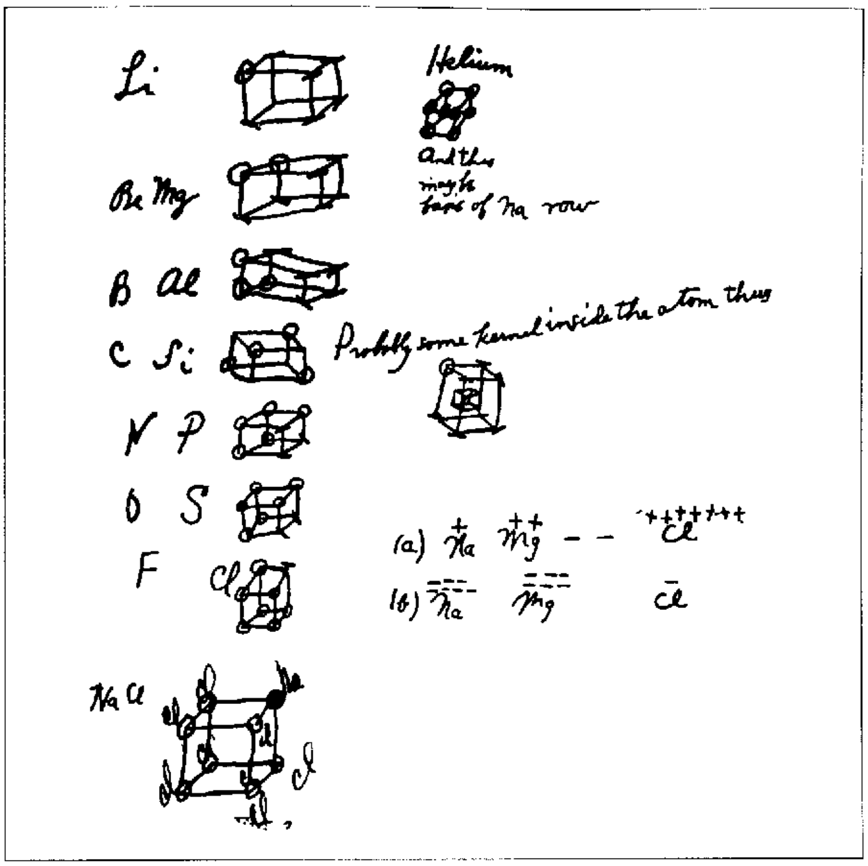


Figure 8.14

G. N. Lewis conceived the octet rule while lecturing to a class of general chemistry students in 1902. This is his original sketch. (G. N. Lewis, *Valence,* Dover Publication, Inc., New York, 1966).

orbitals, these elements typically obey the **octet rule;** they are surrounded by eight electrons. An example is the F_2 molecule, which has the following Lewis structure:

Carbon, nitrogen, oxygen, and fluorine always obey the octet rule in stable molecules.

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}\cdot \longrightarrow :\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}: \longleftarrow \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:$$

F atom with seven valence electrons — F_2 molecule — F atom with seven valence electrons

Note that each fluorine atom in F_2 is, in effect, surrounded by eight electrons, two of which are shared with the other atom. This is a *bonding pair* of electrons, as discussed earlier. Each fluorine atom also has three pairs of electrons not involved in bonding. These are the *lone pairs.*

4. Neon does not form bonds since it already has an octet of valence electrons (it is a noble gas). The Lewis structure is

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Ne}}:$$

Note that only the valence electrons of the neon atom ($2s^22p^6$) are represented by the Lewis structure. The $1s^2$ electrons are core electrons and take no part in chemical reactions.

From the discussion above we can formulate the following rules for writing Lewis structures of molecules containing atoms from the first two periods.

Rules for Writing Lewis Structures

1. Sum the valence electrons from all the atoms. Do not worry about keeping track of which electrons come from which atoms. It is the *total* number of electrons that is important.
2. Use a pair of electrons to form a bond between each pair of bound atoms.
3. Arrange the remaining electrons to satisfy the duet rule for hydrogen and the octet rule for the second-row elements.

To see how these rules are applied, we will draw the Lewis structures of a few molecules. We will first consider the water molecule and follow the rules given above.

1. We sum the *valence* electrons for H_2O as shown:

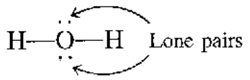
$$\begin{array}{ccccc} 1 & + & 1 & + & 6 = 8 \text{ valence electrons} \\ \nearrow & & \nearrow & & \nearrow \\ \text{H} & & \text{H} & & \text{O} \end{array}$$

2. Using a pair of electrons per bond, we draw in the two O—H single bonds:

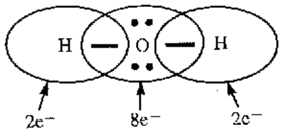
$$\text{H—O—H}$$

Note that *a line instead of a pair of dots is used to indicate each pair of bonding electrons*. This is the standard notation.

3. We distribute the remaining electrons around the atoms to achieve a noble gas electron configuration for each atom. Since four electrons have been used in forming the two bonds, four electrons (8 − 4) remain to be distributed. Hydrogen is satisfied with two electrons (duet rule), but oxygen needs eight electrons to have a noble gas configuration. Thus the remaining four electrons are added to oxygen as two lone pairs. Dots are used to represent the lone pairs:



This is the correct Lewis structure for the water molecule. Each hydrogen has two electrons and the oxygen has eight as shown below.



As a second example, let's write the Lewis structure for carbon dioxide. Summing the valence electrons gives

$$\begin{array}{ccccc} 4 & + & 6 & + & 6 = 16 \\ \nearrow & & \nearrow & & \nearrow \\ \text{C} & & \text{O} & & \text{O} \end{array}$$

After forming a bond between the carbon and each oxygen,

$$\text{O—C—O}$$

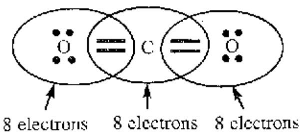
the remaining electrons are distributed to achieve noble gas configurations on each atom. In this case we have twelve electrons (16 − 4) remaining after the bonds are drawn. The distribution of these electrons is determined by a trial-and-error process. We have six pairs of electrons to distribute. Suppose we try three pairs on each oxygen to give

$$:\underset{..}{\ddot{O}}-C-\underset{..}{\ddot{O}}:$$

Is this correct? To answer this we need to check two things:

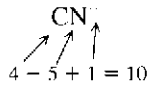
1. The total number of electrons. There are sixteen valence electrons in this structure, which is the correct number.
2. The octet rule for each atom. Each oxygen has eight electrons, but the carbon only has four. This cannot be the correct Lewis structure.

How can we arrange the sixteen available electrons to achieve an octet for each atom? Suppose there are two shared pairs between the carbon and each oxygen:



Now each atom is surrounded by eight electrons, and the total number of electrons is sixteen, as required. This is the correct Lewis structure for carbon dioxide, which has two double bonds.

Finally, let's consider the Lewis structure of the CN^- (cyanide) ion. Summing the valence electrons, we have



Note that the negative charge means an extra electron must be added. After drawing a single bond (C—N), we distribute the remaining electrons to achieve a noble gas configuration for each atom. Eight electrons remain to be distributed. We can try various possibilities, for example:

$$\underset{..}{\ddot{C}}-\underset{..}{\ddot{N}}$$

This structure is incorrect, because C and N have only six electrons each instead of eight. The correct arrangement is

$$[:C\equiv N:]^-$$

(Satisfy yourself that both carbon and nitrogen have eight electrons.)

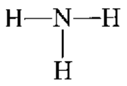
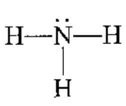
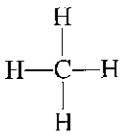
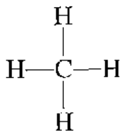
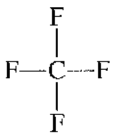
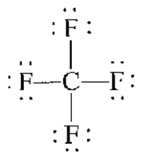
Sample Exercise 8.6

Give the Lewis structure for each of the following:

a. HF **b.** N_2 **c.** NH_3 **d.** CH_4 **e.** CF_4 **f.** NO^+

Solution

In each case we apply the three rules for writing Lewis structures. Recall that lines are used to indicate shared electron pairs and that dots are used to indicate nonbonding pairs (lone pairs). We have the following tabulated results:

	Total valence electrons	Draw single bonds	Calculate number of electrons remaining	Use remaining electrons to achieve noble gas configurations		
					Check	
					Atom	Electrons
a. HF	$1 + 7 = 8$	H—F	6	$\text{H}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{F}}}:$	H F	2 8
b. N_2	$5 + 5 = 10$	N—N	8	$:\text{N}\equiv\text{N}:$	N	8
c. NH_3	$5 + 3(1) = 8$	 $\begin{array}{c}\text{H}-\text{N}-\text{H}\\ \vert\\ \text{H}\end{array}$	2	 $\begin{array}{c}\text{H}-\ddot{\text{N}}-\text{H}\\ \vert\\ \text{H}\end{array}$	H N	2 8
d. CH_4	$4 + 4(1) = 8$	 $\begin{array}{c}\text{H}\\ \vert\\ \text{H}-\text{C}-\text{H}\\ \vert\\ \text{H}\end{array}$	0	 $\begin{array}{c}\text{H}\\ \vert\\ \text{H}-\text{C}-\text{H}\\ \vert\\ \text{H}\end{array}$	H C	2 8
e. CF_4	$4 + 4(7) = 32$	 $\begin{array}{c}\text{F}\\ \vert\\ \text{F}-\text{C}-\text{F}\\ \vert\\ \text{F}\end{array}$	24	 $\begin{array}{c}:\overset{\cdot\cdot}{\text{F}}:\\ \vert\\ :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{F}}}-\text{C}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{F}}}:\\ \vert\\ :\underset{\cdot\cdot}{\text{F}}:\end{array}$	F C	8 8
f. NO^+	$5 + 6 - 1 = 10$	N—O	8	$[:\text{N}\equiv\text{O}:]^+$	N O	8 8

When writing Lewis structures, don't worry about which electrons come from which atoms in a molecule. The best way to look at a molecule is to regard it as a new entity that uses all of the available valence electrons of the atoms to achieve the lowest possible energy.* The valence electrons belong to the molecule, rather than to the individual atoms. Simply distribute all valence electrons so that the various rules are satisfied, without regard to the origin of each particular electron.

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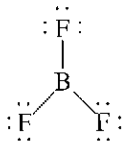
*In a sense this approach corrects for the fact that the localized electron model overemphasizes that a molecule is simply a sum of its parts, that is, that the atoms retain their individual identities in the molecule.

8.11 Exceptions to the Octet Rule

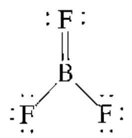
PURPOSE

☐ To show how to write Lewis structures for certain special cases.

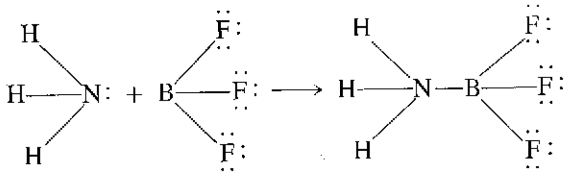
The localized electron model is a simple but very successful model, and the rules we have used for Lewis structures apply to most molecules. However, with such a simple model, some exceptions are inevitable. Boron, for example, tends to form compounds where the boron atom has fewer than eight electrons around it—it does not have a complete octet. Boron trifluoride (BF_3), a gas at normal temperatures and pressures, reacts very energetically with molecules such as water and ammonia that have available electron pairs (lone pairs). The violent reactivity of BF_3 with electron-rich molecules arises because the boron atom is electron-deficient. Boron trifluoride has 24 valence electrons. The Lewis structure that seems most consistent with the properties of BF_3 is



Note that in this structure boron has only six electrons around it. The octet rule for boron can be satisfied by drawing a structure with a double bond, such as



However, since fluorine is much more electronegative than boron, this does not make sense. In fact, experiments indicate that each B—F bond is a single bond in accordance with the first Lewis structure. This structure is also consistent with the reactivity of BF_3 toward electron-rich molecules, for example, toward NH_3 to form H_3NBF_3:



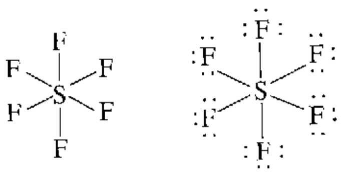
In this stable compound boron has an octet of electrons.

It is characteristic of boron to form molecules where the boron atom is electron-deficient. On the other hand, carbon, nitrogen, oxygen, and fluorine can be counted on to obey the octet rule.

Some atoms exceed the octet rule. This behavior is observed only for those elements in Period 3 of the periodic table and beyond. To see how this arises, we will consider the Lewis structure for sulfur hexafluoride (SF_6). The sum of the valence electrons is

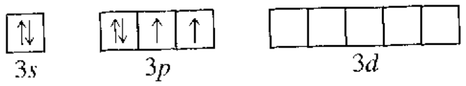
$$6 + 6(7) = 48 \text{ electrons}$$

Indicating the single bonds gives the structure on the left below:



We have used 12 electrons to form the S—F bonds, which leaves 36 electrons. Since fluorine always follows the octet rule, we complete the six fluorine octets to give the structure on the right above. This structure uses all 48 valence electrons for SF_6, but sulfur has 12 electrons around it; that is, sulfur *exceeds* the octet rule. How can this happen?

To answer this question we need to consider the different types of valence orbitals characteristic of second- and third-period elements. The second-row elements have 2*s* and 2*p* valence orbitals, and the third-row elements have 3*s*, 3*p*, and 3*d* orbitals. The 3*s* and 3*p* orbitals fill with electrons in going from sodium to argon, but the 3*d* orbitals remain empty. For example, the valence orbital diagram for a sulfur atom is



The localized electron model assumes that the empty 3*d* orbitals can be used to accommodate extra electrons. Thus the sulfur atom in SF_6 can have 12 electrons around it by using the 3*s* and 3*p* orbitals to hold 8 electrons with the extra 4 electrons placed in the formerly empty 3*d* orbitals. *Second-row elements never exceed the octet rule because they have valence orbitals (2s and 2p) that can hold only eight electrons. Although third-row elements often satisfy the octet rule, they also often exceed it by using their empty d orbitals to share electrons.*

Third-row elements can exceed the octet rule.

When writing the Lewis structure for a molecule, satisfy the octet rule for the atoms first. If electrons remain, place them on the elements having available *d* orbitals. These are the elements in the third period or beyond.

Sample Exercise 8.7

Write the Lewis structure for PCl_5.

Solution

We can follow the same stepwise procedure we used previously.

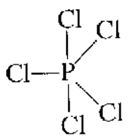
STEP 1

Sum the valence electrons.

$$\underset{\underset{\text{P}}{\uparrow}}{5} + 5\underset{\underset{\text{Cl}}{\uparrow}}{(7)} = 40 \text{ electrons}$$

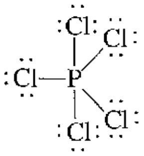
STEP 2

Indicate single bonds between bound atoms.



STEP 3

Distribute the remaining electrons. In this case, 30 electrons (40 − 10) remain. These are used to satisfy the octet rule for each chlorine atom. The final Lewis structure is



Note that phosphorus, which is a third-row element, has exceeded the octet rule by two electrons.

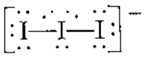
In the PCl_5 and SF_6 molecules, the central atoms (P and S, respectively) must have the extra electrons. However, in molecules having more than one atom that can exceed the octet rule, it is not always clear which atom should have the extra electrons. Consider the Lewis structure for the triiodide ion (I_3^-), which has

$$\underset{\underset{\text{I}}{\uparrow}}{3(7)} + \underset{\underset{1-\text{charge}}{\uparrow}}{1} = 22 \text{ valence electrons}$$

Indicating the single bonds gives I—I—I. At this point 18 electrons (22 − 4) remain. Trial and error will convince you that one of the iodine atoms must exceed the octet rule, but *which* one?

The rule we will follow is that *when it is necessary to exceed the octet rule for one of several third-row (or higher) elements, assume that the extra electrons should be placed on the central atom.*

Thus for I_3^- the Lewis structure is



$$[:\ddot{\underset{..}{\text{I}}}—\ddot{\underset{..}{\text{I}}}—\ddot{\underset{..}{\text{I}}}:]^-$$

where the central iodine exceeds the octet rule. This structure agrees with known properties of I_3^-.

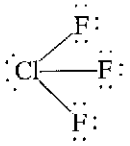
Sample Exercise 8.8

Write the Lewis structure for each molecule or ion:

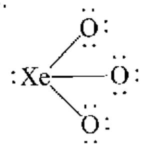
a. ClF_3 **b.** XeO_3 **c.** $RnCl_2$ **d.** ClO_3^- **e.** ICl_4^-

Solution

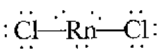
a. The chlorine atom (third row) accepts the extra electrons.



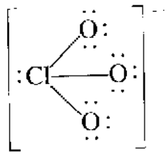
b. All atoms obey the octet rule.



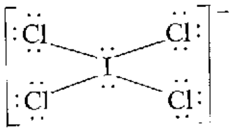
c. Radon, a noble gas in Period 6, accepts the extra electrons.



d. All atoms obey the octet rule.



e. Iodine exceeds the octet rule.



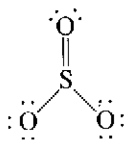
8.12 Resonance

PURPOSE

☐ To illustrate the concept of resonance.

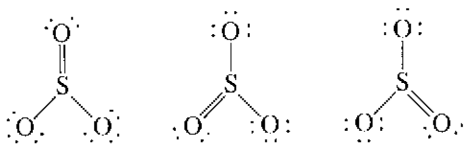
☐ To show how to write resonance structures.

Sometimes more than one valid Lewis structure (one that obeys the rules we have outlined) is possible for a given molecule. Consider the Lewis structure for sulfur trioxide (SO_3), which has 24 valence electrons. To achieve an octet of electrons around each atom, a structure like this is required:



If this structure accurately represents the bonding in SO_3, there should be two types of S—O bonds observed in the molecule: one shorter bond (the double bond) and two identical longer ones (the two single bonds). However, experiments clearly show that SO_3 exhibits only *one* type of S—O bond with a length and strength between those expected for a single bond and a double bond. Thus, although the structure we have shown above is a valid Lewis structure, it does *not* correctly represent the bonding in SO_3. This is a serious problem, and it means that the model must be modified.

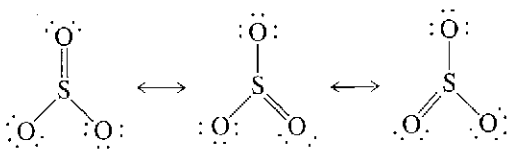
Look again at the proposed Lewis structure for SO_3. There is no reason for choosing a particular oxygen atom to have the double bond. There are really three valid Lewis structures:



Is any of these structures a correct description of the bonding in SO_3? No, because

SO_3 does not have one double and two single bonds—it has three equivalent bonds. We can solve this problem by making the following assumption: the correct description of SO_3 is *not given by any one* of the three Lewis structures, but is given only by the *superposition of all three*.

Sulfur trioxide does not exist as any of the three extreme structures but exists as an average of all three. **Resonance** *occurs when more than one valid Lewis structure can be written for a particular molecule*. The resulting electronic structure of the molecule is given by the average of these **resonance structures.** This situation is usually represented by double-headed arrows as follows:



Note that in all of these resonance structures the arrangement of the nuclei is the same. Only the placement of the electrons differs. The arrows do not indicate that the molecule "flips" from one resonance structure to another. They simply show that the *actual structure is an average of the three resonance structures*.

The concept of resonance is necessary because the localized electron model postulates that electrons are localized between a given pair of atoms. However, nature doesn't really operate this way. Electrons are really delocalized—they can move around the entire molecule. The valence electrons in the SO_3 molecule distribute themselves to provide equivalent S—O bonds. The molecular orbital model, which assumes that electrons are delocalized, can readily handle molecules like SO_3 and does not require the concept of resonance. Resonance is necessary to compensate for the defective assumption of the localized electron model. However, this model is so useful that we retain the concept of localized electrons and add resonance to allow the model to treat molecules like SO_3.

Sample Exercise 8.9

Describe the electron arrangement in the nitrite anion (NO_2^-) using the localized electron model.

Solution

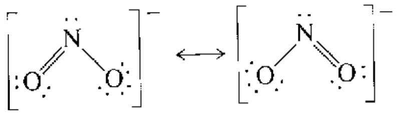
We will follow the usual procedure for obtaining the Lewis structure for the NO_2^- ion.

In NO_2^- there are $5 + 2(6) + 1 = 18$ valence electrons.

Indicating the single bonds gives the structure

O—N—O

The remaining 14 electrons $(18 - 4)$ can be distributed to produce these structures:



This is a resonance situation. Two equivalent Lewis structures can be drawn. *The electronic structure of the molecule is not correctly represented by either resonance structure but by the average of the two*. There are two equivalent N—O bonds, each one intermediate between a single and double bond.

Odd-Electron Molecules

Relatively few molecules formed from nonmetals contain odd numbers of electrons. One common example is nitric oxide (NO) which is formed when nitrogen and oxygen gases react at the high temperatures in automobile engines. Nitric oxide is emitted into the air, where it immediately reacts with oxygen to form gaseous nitrogen dioxide (NO_2), another odd-electron molecule.

Since the localized electron model is based on pairs of electrons, it does not handle odd-electron cases in a natural way. To treat odd-electron molecules, a more sophisticated model is needed. The usual choice is the molecular orbital model, which has no problems with odd numbers of electrons.

The molecular orbital model is discussed in Section 9.2.

8.13

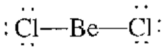
Molecular Structure: The VSEPR Model

PURPOSE

☐ To describe how molecular geometry can be predicted from the number of electron pairs.

The structures of molecules play a very important role in determining their chemical properties. As we will see later, this is particularly important for biological molecules; a slight change in the structure of a large biomolecule can completely destroy its usefulness to a cell or may even change the cell from a normal one to a cancerous one.

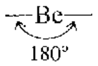
Many accurate methods now exist for determining **molecular structure,** the three-dimensional arrangement of atoms in a molecule. These methods must be used if precise information about structure is required. However, it is often useful to be able to predict the approximate molecular structure of a molecule. In this section we consider a simple model that allows us to do this. This model, called the **valence shell electron pair repulsion (VSEPR) model,** is useful in predicting the geometries of molecules formed from nonmetals. The main postulate of this model is that *the structure around a given atom is determined principally by minimizing electron-pair repulsions.* The idea here is that the bonding and nonbonding pairs around a given atom will be positioned as far apart as possible. To see how this model works, we will first consider the molecule $BeCl_2$, which has the Lewis structure



$$:\ddot{\underset{..}{Cl}}-Be-\ddot{\underset{..}{Cl}}:$$

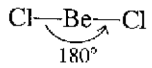
Note that there are two pairs of electrons around the beryllium atom. What arrangement of these electron pairs allows them to be as far apart as possible to minimize the repulsions? Clearly, the best arrangement places the pairs on opposite sides of the beryllium atom at 180° from each other:

$BeCl_2$ has only four electrons around Be and is expected to be very reactive with electron-pair donors.

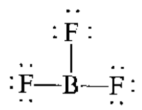


This is the maximum possible separation for two electron pairs. Once we have determined the optimum arrangement of the electron pairs around the central atom, we can specify the molecular structure of $BeCl_2$, that is, the positions of the atoms.

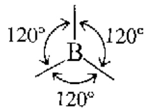
Since each electron pair on beryllium is shared with a chlorine atom, the molecule has a **linear structure** with a 180° bond angle:



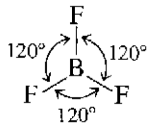
Next, let's consider BF_3, which has the Lewis structure



Here the boron atom is surrounded by three pairs of electrons. What arrangement will minimize the repulsions? The electron pairs are farthest apart at angles of 120°:

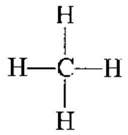


Since each of the electron pairs is shared with a fluorine atom, the molecular structure will be

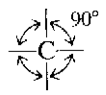


This is a planar (flat) and triangular molecule, which is commonly described as a **trigonal planar structure.**

Next, let's consider the methane molecule, which has the Lewis structure

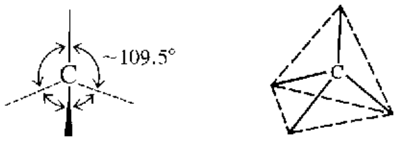


There are four pairs of electrons around the central carbon atom. What arrangement of these electron pairs best minimizes the repulsions? First, let's try a square planar arrangement:

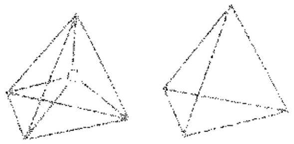


The carbon atom and the electron pairs are centered in the plane of the paper, and the angles between the pairs are all 90°.

Is there another arrangement with angles greater than 90° that would put the electron pairs even further away from each other? The answer is yes. The **tetrahedral arrangement** has angles of approximately 109.5°:



It can be shown that this is the maximum possible separation of four pairs around a given atom. This means that *whenever four pairs of electrons are present around an atom, they should always be arranged tetrahedrally.*



A tetrahedron has four equal triangular faces.

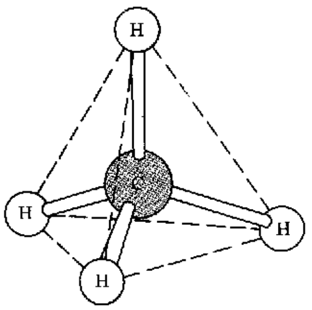


Figure 8.15

The molecular structure of methane. The tetrahedral arrangement of electron pairs produces a tetrahedral arrangement of hydrogen atoms.

Now that we have the electron-pair arrangement that gives the least repulsion, we can determine the positions of the atoms and thus the molecular structure of CH_4. In methane each of the four electron pairs is shared between the carbon atom and a hydrogen atom. Thus the hydrogen atoms are placed as in Fig. 8.15, and the molecule has a tetrahedral structure with the carbon atom at the center.

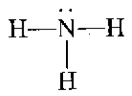
Recall that the main idea of the VSEPR model is to find the arrangement of electron pairs around the central atom that minimizes the repulsions. Then we can determine the molecular structure from knowing how the electron pairs are shared with the peripheral atoms. Use the following steps to predict the structure of a molecule using the VSEPR model.

- Draw the Lewis structure for the molecule.
- Count the electron pairs and arrange them in the way that minimizes repulsion (that is, put the pairs as far apart as possible).
- The positions of the atoms are determined from the way the electron pairs are shared.
- The name of the molecular structure is determined from the positions of the *atoms*.

We will predict the structure of ammonia (NH_3) using this stepwise approach.

STEP 1

Draw the Lewis structure:



$$\mathrm{H{-}\overset{\cdot\cdot}{N}{-}H}\atop{\quad\mathrm{|}\atop\mathrm{H}}$$

STEP 2

Count the pairs of electrons and arrange them to minimize repulsions. The NH_3 molecule has four pairs of electrons: three bonding pairs, and one nonbonding pair. From the discussion of the methane molecule, we know that the best arrangement of four electron pairs is a tetrahedral structure as shown in Fig. 8.16(a).

STEP 3

Determine the positions of the atoms. The three H atoms share electron pairs as shown in Fig. 8.16(b).

STEP 4

Name the molecular structure. It is very important to recognize that the name of the molecular structure is always based on the *positions of the atoms*. The placement of the electron pairs determines the structure, but the name is based on the positions of the atoms. Thus it is incorrect to say that the NH_3 molecule is tetrahedral. It has a tetrahedral arrangement of electron pairs but not a tetrahedral arrangement of atoms. The molecular structure of ammonia is a **trigonal pyramid** (one side is different from the other three) rather than a tetrahedron.

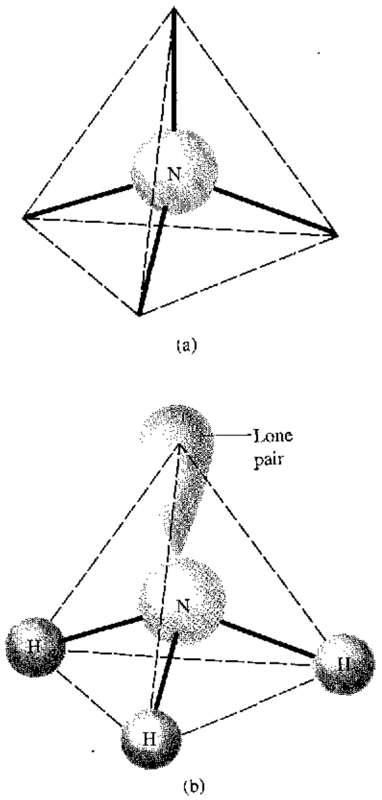


Figure 8.16

(a) The tetrahedral arrangement of electron pairs around the nitrogen atom in the ammonia molecule. (b) Three of the electron pairs around nitrogen are shared with hydrogen atoms as shown and one is a lone pair. Although the arrangement of *electron pairs* is tetrahedral, as in the methane molecule, the hydrogen atoms in the ammonia molecule occupy only three corners of the tetrahedron. A lone pair occupies the fourth corner.

Sample Exercise 8.10

Describe the molecular structure of the water molecule.

Solution

The Lewis structure for water is

$$\mathrm{H}-\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}-\mathrm{H}$$

There are four pairs of electrons: two bonding pairs, and two nonbonding pairs. To minimize repulsions, these are best arranged in a tetrahedral structure as shown in Fig. 8.17(a). Although H_2O has a tetrahedral arrangement of electron pairs, it is not a tetrahedral molecule. The atoms in the H_2O molecule form a V shape as shown in Fig. 8.17(b) and (c).

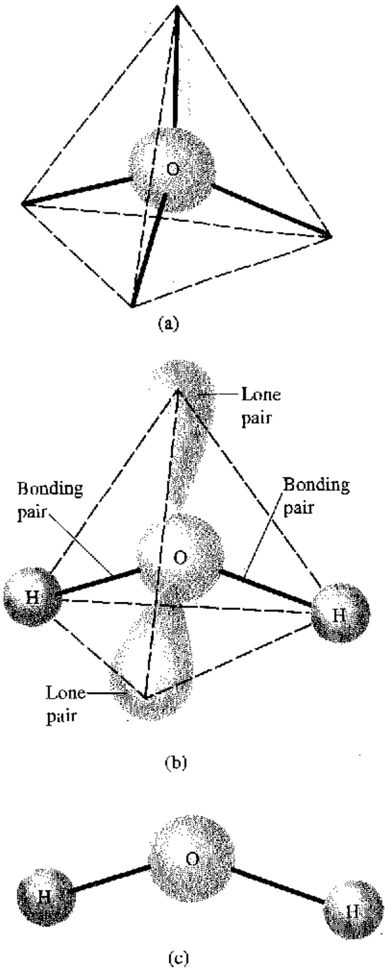


Figure 8.17

(a) The tetrahedral arrangement of the four electron pairs around oxygen in the water molecule. (b) Two of the electron pairs are shared between oxygen and the hydrogen atoms and two are lone pairs. (c) The V-shaped molecular structure of the water molecule.

From Sample Exercise 8.10 we see that the H_2O molecule is V-shaped, or bent, because of the presence of the lone pairs. If no lone pairs were present, the molecule would be linear, and the polar bonds would cancel and the molecule would have no dipole moment. This would make water very different from the polar substance so familiar to us.

From the previous discussion we would predict that the H—X—H bond angle (where X is the central atom) in CH_4, NH_3, and H_2O should be the tetrahedral angle of 109.5°. Experimental studies, however, have shown that the bond angles are those given in Fig. 8.18. What significance do these results have for the VSEPR model? One possible point of view is that we should be pleased to have the observed angles so close to the tetrahedral angle. The opposite view is that the deviations are significant enough to require modification of the simple model so that it can more accurately handle similar cases. We will take the latter view.

Let us examine the following data:

	CH_4	NH_3	H_2O
Number of lone pairs	0	1	2
Bond angle	109.5°	107°	104.5°

One interpretation of the trend observed here is that lone pairs require more space than bonding pairs; in other words, as the number of lone pairs increases, the bonding pairs are increasingly squeezed together.

This interpretation seems to make physical sense if we think in the following terms. A bonding pair is shared between two nuclei and the electrons can be close to either nucleus. They are relatively confined between the two nuclei. A lone pair is

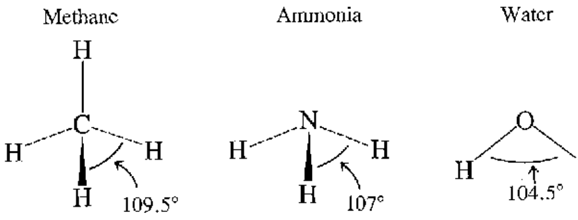


Figure 8.18

The bond angles in the CH_4, NH_3, and H_2O molecules. Note that although each of these molecules has four pairs of electrons around the central atom, the bond angle between bonding pairs decreases as the number of lone pairs increases.

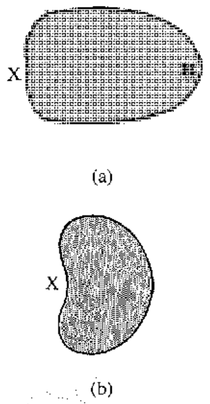


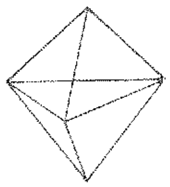
Figure 8.19

(a) In a bonding pair of electrons, the electrons are shared by two nuclei. (b) In a lone pair, both electrons must be close to a single nucleus and tend to take up more of the space around that atom.

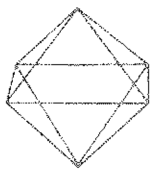
localized on only one nucleus and both electrons will be close only to that nucleus, as shown schematically in Fig. 8.19. These pictures help us understand why a lone pair may require more space near an atom than a bonding pair.

As a result of these observations, we make the following addition to the original postulate of the VSEPR model: *lone pairs require more room than bonding pairs and tend to compress the angles between the bonding pairs.*

So far we have considered cases with two, three, and four electron pairs around the central atom. These are summarized in Table 8.6. For five pairs of electrons, there are several possible choices. The one that produces minimum repulsion is a *trigonal bipyramid.* Note from Table 8.6 that this arrangement has two different angles, 90° and 120°. As the name suggests, the structure formed by this arrangement of pairs consists of two trigonal-based pyramids that share a common base. Six pairs of electrons can best be arranged *octahedrally* around a given atom with 90° angles, as shown in Table 8.6.



A trigonal bipyramid.



An octahedron has six equal triangular faces.

Arrangements of Electron Pairs Around an Atom Yielding Minimum Repulsion

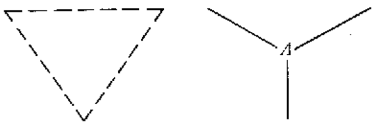
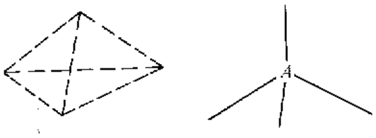
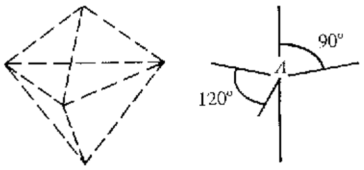
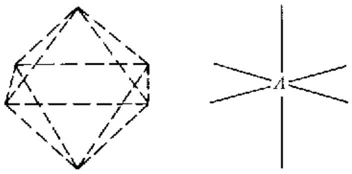
Number of electron pairs	Geometric arrangement of electron pairs	
2	Linear	
3	Trigonal planar	
4	Tetrahedral	
5	Trigonal bipyramidal	
6	Octahedral	

Table 8.6

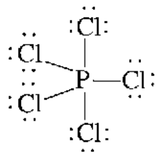
In order to use the VSEPR model to determine the geometric structures of molecules, you should memorize the relationships between the number of electron pairs and their best arrangement.

Sample Exercise 8.11

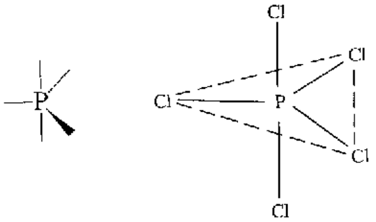
When phosphorus reacts with excess chlorine gas, the compound phosphorus pentachloride (PCl_5) is formed. In the gaseous and liquid states, this substance consists of PCl_5 molecules, but in the solid state it consists of a 1:1 mixture of PCl_4^+ and PCl_6^- ions. Predict the geometric structures of PCl_5, PCl_4^+, and PCl_6^-.

Solution

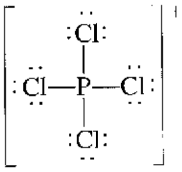
As shown previously, the Lewis structure for PCl_5 is



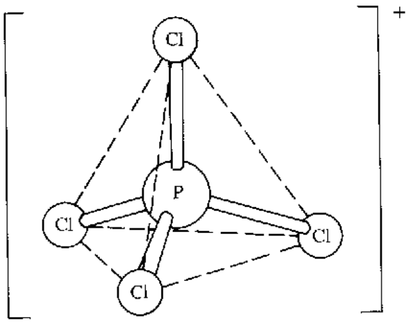
Five pairs of electrons around the phosphorus atom require a trigonal bipyramidal arrangement (see Table 8.6) as shown on the left below. When the chlorine atoms are included, a trigonal bipyramidal molecule results, as shown on the right.



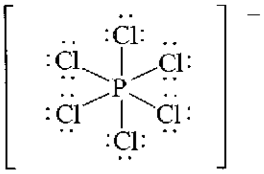
The Lewis structure for the PCl_4^+ ion [5 + 4(7) − 1 = 32 valence electrons] is:



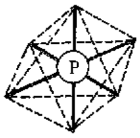
There are four pairs of electrons surrounding the phosphorus atom in the PCl_4^- ion, which requires a tetrahedral arrangement of the pairs, as shown below on the left. Since each pair is shared with a chlorine atom, a tetrahedral PCl_4^+ cation results.

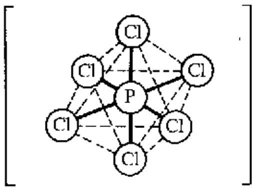


The Lewis structure for PCl_6^- [5 + 6(7) + 1 = 48 valence electrons] is



Since phosphorus is surrounded by six pairs of electrons, an octahedral arrangement is required to minimize repulsions, as shown below on the left. Since each electron pair is shared with a chlorine atom, an octahedral PCl_6^- anion is predicted.



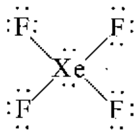


Sample Exercise 8.12

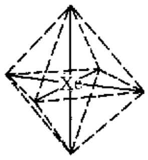
Because the noble gases have filled *s* and *p* valence orbitals, they were not expected to be chemically reactive. In fact, for many years these elements were called *inert gases* because of this supposed inability to form any compounds. However, in the early 1960s several compounds of krypton, xenon, and radon were synthesized. For example, a team at the Argonne National Laboratory produced the stable colorless compound xenon tetrafluoride (XeF_4). Predict its structure.

Solution

The Lewis structure for XeF_4 is



The xenon atom in this molecule is surrounded by six pairs of electrons, which means an octahedral arrangement:



The structure predicted for this molecule will depend on how the lone pairs and bonding pairs are arranged. Consider the two possibilities shown in Fig. 8.20. The bonding pairs are indicated by the presence of the fluorine atoms. Since the structure predicted differs in the two cases, we must decide which of these arrangements

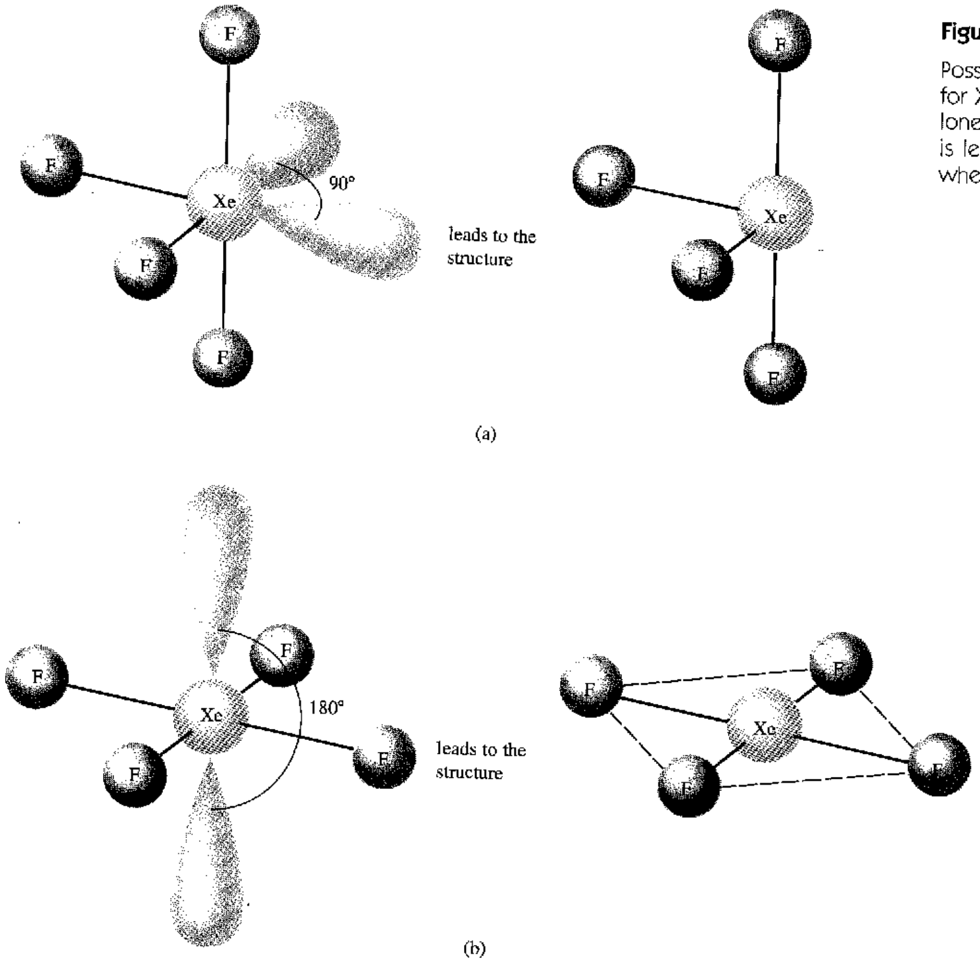


Figure 8.20

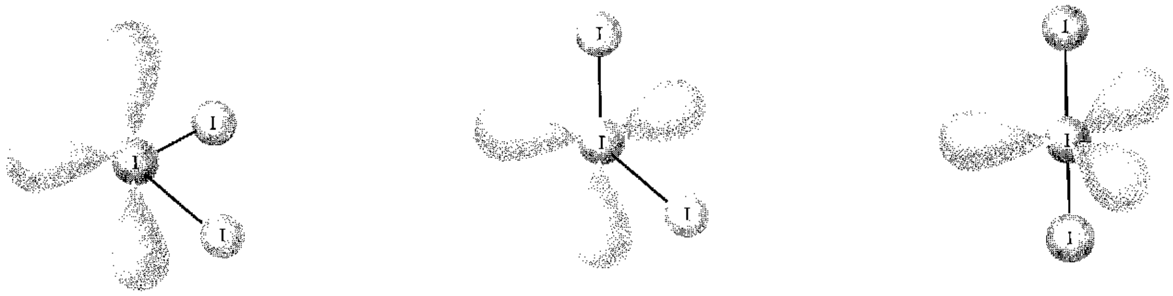
Possible electron pair arrangements for XeF_4. Since arrangement (a) has lone pairs at 90° from each other, it is less favorable than arrangement (b), where the lone pairs are at 180°.

is preferable. The key is to look at the lone pairs. In the structure in part (a) the lone pair–lone pair angle is 90°; in the structure in part (b) the lone pairs are separated by 180°. Since lone pairs require more room than bonding pairs, a structure with two lone pairs at 90° is unfavorable. Thus the arrangement in Fig. 8.20(b) is preferred, and the molecular structure is predicted to be square planar. Note that this molecule is *not* described as being octahedral. There is an *octahedral arrangement of electron pairs*, but the *atoms* form a *square planar* structure.

We can further illustrate the use of the VSEPR model for molecules or ions with lone pairs by considering the triiodide ion (I_3^-). The Lewis structure for I_3^- is

$$\left[:\underset{..}{\ddot{I}}-\underset{..}{\ddot{I}}-\underset{..}{\ddot{I}}:\right]^-$$

The central iodine atom has five pairs around it, which requires a trigonal bipyramidal arrangement. Several possible arrangements of the lone pairs are shown in Fig.



(a) (b) (c)

Figure 8.21

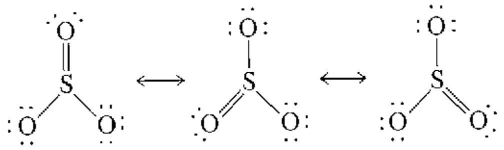
Three possible arrangements of the electron pairs in the I_3^- ion. Arrangement (c) is preferred because there are no 90° lone pair–lone pair interactions.

8.21. Note that structures (a) and (b) have lone pairs at 90°, whereas in (c) all lone pairs are at 120°. Thus structure (c) is preferred. The resulting molecular structure for I_3^- is linear.

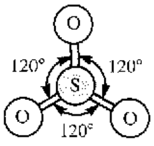
$$[\mathrm{I{-}I{-}I}]^-$$

The VSEPR Model and Multiple Bonds

So far in our treatment of the VSEPR model, we have not considered any molecules with multiple bonds. To see how these molecules are handled by this model, let's consider the SO_3 molecule, which requires three resonance structures to describe its electronic structure:



The SO_3 molecule is known to be planar with 120° bond angles.



This planar structure is the one expected for three pairs of electrons around a central atom, which means that *a double bond should be counted as one effective pair* in using the VSEPR model. This makes sense because the two pairs of electrons involved in the double bond are *not* independent pairs. Both of the electron pairs must be in the space between the nuclei of the two atoms in order to form the double bond. In other words, the double bond acts as one center of electron density to repel the other pairs of electrons. The same holds true for triple bonds. This leads us to another general rule: *for the VSEPR model multiple bonds count as one effective electron pair.*

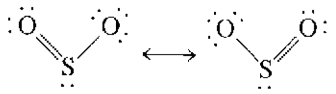
The molecular structure of sulfur trioxide also shows us one more important point: *when a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular structure using the VSEPR model.* These rules are illustrated in Sample Exercise 8.13.

Sample Exercise 8.13

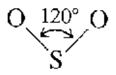
Predict the molecular structure of the sulfur dioxide molecule.

Solution

First, we must determine the Lewis structure for the SO_2 molecule, which has 18 valence electrons. The resonance structures are



To determine the molecular structure, we must count the electron pairs around the sulfur atom. In each resonance structure the sulfur has one lone pair, one pair in a single bond, and one double bond. Counting the double bond as one pair yields three effective pairs around the sulfur. According to Table 8.6, a trigonal planar arrangement is required, which yields a V-shaped molecule:

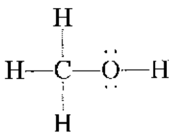


Thus the structure of the SO_2 molecule is expected to be V-shaped, with a 120° bond angle.

It should be noted at this point that lone pairs that are oriented at least 120° from other pairs do not produce significant distortions of bond angles. For example, the angle in the SO_2 molecule is actually quite close to 120°. We will follow the general principle that *a 120° angle provides lone pairs with enough space so that distortions do not occur. Angles less than 120° are distorted when lone pairs are present.*

Molecules Containing No Single Central Atom

So far we have considered molecules consisting of one central atom surrounded by other atoms. The VSEPR model can be readily extended to more complicated molecules, such as methanol (CH_3OH). This molecule is represented by the following Lewis structure:



$$\mathrm{H-\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-\ddot{\underset{\cdot\cdot}{O}}-H}$$

The molecular structure can be predicted from the arrangement of pairs around the carbon and oxygen atoms. Note that there are four pairs of electrons around the

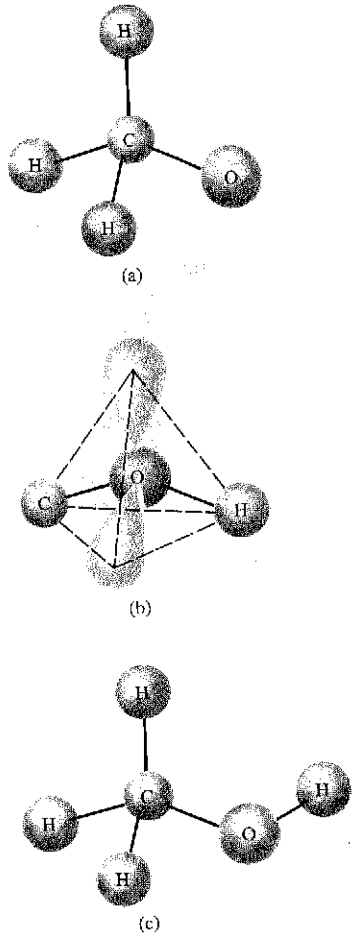


Figure 8.22

The molecular structure of methanol. (a) The arrangement of electron pairs and atoms around the carbon atom. (b) The arrangement of bonding and lone pairs around the oxygen atom. (c) The molecular structure.

carbon, which calls for a tetrahedral arrangement as shown in Fig. 8.22(a). The oxygen also has four pairs, which requires a tetrahedral arrangement. However, in this case the tetrahedron will be slightly distorted by the space requirements of the lone pairs [Fig. 8.22(b)]. The overall geometric arrangement for the molecule is shown in Fig. 8.22(c).

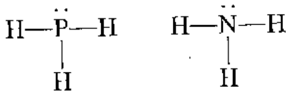
Summary of the VSEPR Model

The rules for using the VSEPR model to predict molecular structure are

1. Determine the Lewis structure(s) for the molecule.
2. For molecules with resonance structures, use any of the structures to predict the molecular structure.
3. Sum the electron pairs around the central atom.
4. In counting pairs, count each multiple bond as a single effective pair.
5. The arrangement of the pairs is determined by minimizing electron pair repulsions. These arrangements are shown in Table 8.6.
6. Lone pairs require more space than bonding pairs. Choose an arrangement that gives the lone pairs as much room as possible. Recognize that the lone pairs may produce a slight distortion of the structure at angles less than 120°.

The VSEPR Model—How Well Does It Work?

The VSEPR model is very simple. There are only a few rules to remember, yet the model correctly predicts the molecular structures of most molecules formed from nonmetallic elements. Molecules of any size can be treated by applying the VSEPR model to each appropriate atom (those bonded to at least two other atoms) in the molecule. Thus we can use this model to predict the structures of molecules with hundreds of atoms. It does, however, fail in a few instances. For example, phosphine (PH_3), which has a Lewis structure analogous to that of ammonia,



$$\begin{array}{c} \mathrm{H{-}\ddot{P}{-}H} \\ | \\ \mathrm{H} \end{array} \qquad \begin{array}{c} \mathrm{H{-}\ddot{N}{-}H} \\ | \\ \mathrm{H} \end{array}$$

would be predicted to have a molecular structure similar to that for NH_3 with bond angles of approximately 107°. However, the bond angles of phosphine are actually 94°. There are ways of explaining this structure, but more rules have to be added to the model.

This again illustrates the point that simple models are bound to have exceptions. In introductory chemistry we want to use simple models that fit the majority of cases; we are willing to accept a few failures rather than complicate the model. The amazing thing about the VSEPR model is that such a simple model predicts correctly the structures of so many molecules.

CHEMICAL IMPACT

CHEMICAL STRUCTURE AND COMMUNICATION: SEMIOCHEMICALS

In this chapter we have stressed the importance of being able to predict the three-dimensional structure of a molecule. Molecular structure is important because of its effect on chemical reactivity. This is especially true in biological systems, where reactions must be efficient and highly specific. Among the hundreds of types of molecules in the fluids of a typical biological system, the appropriate reactants must find and react only with each other—they must be very discriminating. This specificity depends largely on structure. The molecules are constructed so that only the appropriate partners can approach each other in a way that allows reaction.

Another area where molecular structure is central is in the use of molecules as a means of communication. Examples of chemical communication occur in humans in the conduction of nerve impulses across synapses, the control of the manufacture and storage of key chemicals in cells, and the senses of smell and taste. Plants and animals also use chemical communication. For example, ants lay down a chemical trail so that other ants can find a particular food supply. Ants also warn their fellow workers of approaching danger by emitting certain chemicals.

Molecules convey messages by fitting into appropriate receptor sites in a very specific way, which is determined by their structure. When a molecule occupies a receptor site, chemical processes are stimulated that produce the appropriate response. Sometimes receptors can be fooled, as in the use of artificial sweeteners—molecules fit the sites on the taste buds that stimulate a ''sweet'' response in the brain, but they are not metabolized in the same way as natural sugars. Similar deception is useful in insect control. If an area is sprayed with synthetic female sex attractant molecules, the males of that species become so confused that mating does not occur.

A *semiochemical* is a molecule that delivers a message between members of the same or different species of plant or animal. There are three groups of these chemical messengers: allomones, kairomones, and pheromones. Each is of great ecological importance.

An *allomone* is defined as a chemical that somehow gives adaptive advantage to the producer. For example, leaves of the black walnut tree contain a herbicide, juglone, that appears after the leaves fall to the ground. Juglone is not toxic to grass or certain grains, but it is effective against plants such as apple trees that would compete for the available water and food supplies.

Antibiotics are also allomones since the microorganisms produce them to inhibit other species from growing near them.

Many plants produce bad-tasting chemicals to protect themselves from plant-eating insects and animals. The familiar compound nicotine deters animals from eating the tobacco plant. The millipede sends an unmistakable ''back off'' message by squirting a predator with benzaldehyde and hydrogen cyanide.

Defense is not the only use of allomones, however. Flowers use scent to attract pollinating insects. Honeybees, for instance, are guided to alfalfa flowers by a series of sweet-scented compounds.

Kairomones are chemical messengers that bring advantageous news to the receiver, and the floral scents are kairomones from the honeybees' viewpoint. Many predators are guided by kairomones emitted by their food. For example, apple skins exude a chemical that attracts the codling moth larva. In some cases kairomones help the underdog. Certain marine mollusks can pick up the ''scent'' of their predators, the sea stars, and make their escape.

Pheromones are chemicals that affect receptors of the same species as the donor. That is, they are specific within a species. *Releaser pheromones* cause an immediate reaction in the receptor, and *primer pheromones* cause long-term effects. Examples of releaser pheromones are the sex attractants of insects, generated in some species by the males and in others by the females. Sex pheromones have also been found in plants and mammals.

Alarm pheromones are highly volatile compounds (ones easily

CHEMICAL IMPACT

changed to a gas) released to warn of danger. Honeybees produce isoamyl acetate ($C_7H_{14}O_2$) in their sting glands. Because of its high volatility, this compound does not linger after the state of alert is over. Social behavior in insects is characterized by the use of *trail pheromones,* which are used to indicate a food source. Social insects such as bees, ants, wasps, and termites use these substances. Since trail pheromones are less volatile compounds, the indicators persist for some time.

Primer pheromones, which cause long-term behavioral changes, are harder to isolate and identify. One example, however, is the "queen substance" produced by queen honeybees. All the eggs in a colony are laid by one queen bee. If she is removed from the hive or dies, the worker bees are activated by the absence of the queen substance and begin to feed royal jelly to bee larvae in order to raise a new queen. The queen substance also prevents the development of the workers' ovaries so that only the queen herself can produce eggs.

Many studies of insect pheromones are now underway in the hope that they will provide a method of controlling insects that is more efficient and safer than the current chemical pesticides. Pest control will be discussed in Chapter 24.

Summary

Chemical bonds hold groups of atoms together. Bonding occurs when a group of atoms can lower its total energy by aggregating. Bonds can be classified into several types. In an ionic bond there is a transfer of electrons to form ions; in a covalent bond electrons are shared. Between these extremes, in a polar covalent bond electrons are shared unequally. The percent ionic character of the bond in a diatomic molecule XY can be defined as

$$\text{Percent ionic character} = \left(\frac{\text{measured dipole moment of X} - \text{Y}}{\text{calculated dipole moment of X}^+\text{Y}^-}\right) \times 100$$

Electronegativity is defined as the relative ability of an atom in a molecule to attract the electrons shared in a bond. The electronegativity difference of the atoms involved in a bond determines the polarity of that bond. The spatial arrangement of polar bonds determines the overall polarity, or dipole moment, of a molecule.

Stable molecules usually contain atoms that have filled valence orbitals. Nonmetals bonding to each other achieve noble gas configurations in their valence orbitals by covalent bonding. A nonmetal and a representative group metal achieve the same result by transferring electrons to form ions.

Ions have significantly different sizes from their parent atoms. Cations are smaller because the parent atom has lost electrons to become an ion. Anions, because they have more electrons than the parent atom, are larger. In general, ion size increases going down a group. Isoelectronic ions (having the same number of electrons) decrease in size with increasing *Z* values.

Lattice energy is the change in energy that takes place when separated gaseous ions are packed together to form an ionic solid. Bond energy, the energy necessary to break a covalent bond, varies with the number of shared electron pairs. A single bond involves one electron pair; a double bond, two electron pairs; and a triple bond, three electron pairs. Bond energies can be used to calculate the enthalpy change for a reaction.

The Lewis structure of a molecule shows how the valence electrons are arranged among the atoms. The duet rule for hydrogen and the octet rule for second-row elements reflect the observation that atoms tend to fill their valence orbitals. Elements in the third row and beyond can exceed the octet rule because of the availability of empty *d* orbitals.

Sometimes more than one valid Lewis structure can be drawn for the same molecule, which is accounted for by the concept of resonance. The actual electronic structure is represented by the superposition of the resonance structures in such cases.

The VSEPR model is very useful in predicting the geometries of molecules formed from nonmetals. The principal postulate of this model is that the structure around a given atom is determined by minimizing electron-pair repulsions.

Key Terms

bond energy (8.1)
ionic bonding
Coulomb's law
ionic compound
bond energy
bond length
covalent bonding
polar covalent bond
electronegativity (8.2)
dipole moment (8.3)
isoelectronic ions (8.4)
lattice energy (8.5)
single bond (8.8)
double bond
triple bond
molecular orbital (MO) model (8.9)
molecular orbital
delocalization
localized electron (LE) model
lone pair
bonding pair
Lewis structure (8.10)
duet rule
octet rule
resonance (8.12)
resonance structure
molecular structure (8.13)
valence shell electron pair repulsion (VSEPR) model
linear structure
trigonal planar structure
tetrahedral structure
trigonal pyramidal structure
trigonal bipyramidal structure
octahedral structure
square planar structure

Exercises

Chemical Bonds and Electronegativity

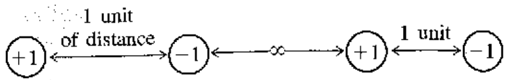
1. Tell the difference between the following pairs of terms:
   a. electronegativity and electron affinity
   b. covalent bond and polar covalent bond
   c. polar covalent bond and ionic bond

2. Use Coulomb's law,

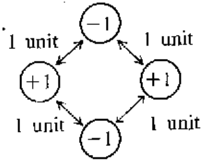
$$E = k\left(\frac{Q_1Q_2}{r}\right)$$

to calculate the energy of interaction for the following two arrangements of charges in arbitrary units. Assume a value of $k = 1.0$.

a.



b.



3. Without using Fig. 8.3, predict the order of increasing electronegativity in each of the following groups of elements:
   a. C, N, O
   b. S, Se, Cl
   c. Si, Ge, Sn
   d. Tl, S, Ge

4. Without using Fig. 8.3, predict which bond in each of the following groups will be the most polar:
   a. C—F, Si—F, Ge—F
   b. P—Cl, S—Cl
   c. S—F, S—Cl, S—Br
   d. Ti—Cl, Si—Cl, Ge—Cl
   e. C—H, Si—H, Sn—H
   f. Al—Br, Ga—Br, In—Br, Tl—Br

5. Repeat Exercises 3 and 4. This time use the values for the electronegativities of the elements given in Fig. 8.3. Are there any differences in your answers?

6. a. Although not often used, the electronegativities of the noble gases are quite high. (Ne = 4.4; Ar = 4.0; Kr = 2.9; Xe = 2.6) Explain these high values relative to those of the other elements using an alternative definition of the electronegativity

$$\text{Electronegativity} \propto (\text{I.E.} - \text{E.A.})$$

where I.E. is the ionization energy and E.A. is the electron affinity using the sign convention of this book.

   b. Elemental fluorine (F_2) reacts directly with xenon to produce three different compounds: XeF_2, XeF_4, XeF_6. Would you expect any of the other noble gases to react with fluorine?

Ionic Compounds

7. For each of the following groups, place the atoms and ions in order of decreasing size:
   a. Cu, Cu^+, Cu^{2+}
   b. Ni^{2+}, Pd^{2+}, Pt^{2+}
   c. O^{2-}, S^{2-}, Se^{2-}
   d. La^{3+}, Eu^{3+}, Gd^{3+}, Yb^{3+}
   e. Te^{2-}, I^-, Xe, Cs^+, Ba^{2+}, La^{3+}

8. Write electron configurations for the following ions: Mg^{2+}, Cr^{3+}, Zn^{2+}, Sn^{2+}, Sn^{4+}, Se^{2-}, I^-.

9. Which of the following ions have noble gas electron configurations?
   a. Fe^{2+}, Fe^{3+}, Sc^{3+}, Co^{3+}
   b. Tl^+, Te^{2-}, Cr^{3+}
   c. Pu^{4+}, Ce^{4+}, Ti^{4+}
   d. Ba^{2+}, Pt^{2+}, Mn^{2+}

10. Define the term *isoelectronic*. When comparing sizes of ions of elements in the same period in the periodic table, why is it advantageous to compare isoelectronic species?

11. Which compound in each of the following pairs of ionic substances has the greatest lattice energy? Justify your answers.
   a. NaCl, KCl
   b. LiF, LiCl
   c. $Mg(OH)_2$, MgO
   d. $Fe(OH)_2$, $Fe(OH)_3$

12. Some of the important properties of ionic compounds are
   I. Low electrical conductivity as solids, and high conductivity in solution or when molten
   II. Relatively high melting and boiling points
   III. Brittleness
   IV. Solubility in polar solvents

   How does the concept of ionic bonding discussed in this chapter account for these properties?

13. Use the following data to estimate ΔH_f^0 for sodium chloride.

$$Na(s) + \tfrac{1}{2}\,Cl_2(g) \rightarrow NaCl(s)$$

Lattice energy	−757 kJ/mol
Ionization energy for Na	495 kJ/mol
Electron affinity of Cl	−348 kJ/mol
Bond energy of Cl_2	239 kJ/mol
Enthalpy of sublimation for Na	108 kJ/mol

14. Give three ions that are isoelectronic with the krypton atom.

15. Consider the following energy changes:

	ΔH(kJ/mol)
$Mg(g) \rightarrow Mg^+(g) + e^-$	737.7
$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$	1450.7
$O(g) + e^- \rightarrow O^-(g)$	−141
$O^-(g) + e^- \rightarrow O^{2-}(g)$	+780

a. Magnesium oxide exists as $Mg^{2+}O^{2-}$ and not as Mg^+O^-. Explain.
b. What simple experiment could be done to confirm that magnesium oxide does not exist as Mg^+O^-?

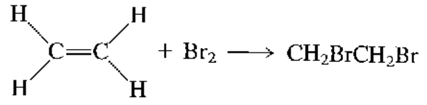
16. Predict the empirical formulas of the ionic compounds formed from the following pairs of elements. Name each compound.
a. Li and N
b. Ga and O
c. Rb and Cl
d. Ba and S

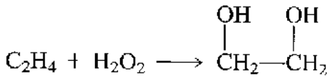
17. Using Fig. 8.13 and the electronegativity values from Fig. 8.3, predict the percent ionic character for the following compounds.

a. $TiCl_4$
b. H_2S
c. CsH
d. $SbBr_3$
e. SnF_2
f. PbO
g. Fe_2O_3
h. $AlCl_3$
i. MgS
j. SiO_2
k. CS_2
l. SO_2

Bond Energies

18. Use bond energy values in Table 8.4 to estimate ΔH for each of the following reactions in the gas phase:

a.


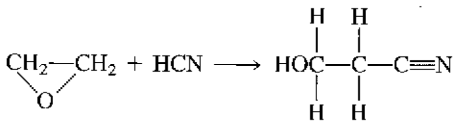
b.


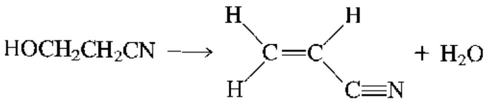
$$C_2H_4 + H_2O_2 \longrightarrow \underset{}{\overset{OH}{CH_2}}-\overset{OH}{CH_2}$$

c. $H_2 + Cl_2 \rightarrow 2HCl$
d. $N_2 + 3H_2 \rightarrow 2NH_3$

19. Compare your answers from Exercise 18(c) and (d) to ΔH values calculated for each reaction from standard enthalpies of formation in Appendix 4. Do enthalpy changes calculated from bond energies give a reasonable estimate of the actual values?

20. Three processes that have been used for the industrial manufacture of acrylonitrile, an important chemical used in the manufacture of plastics, synthetic rubber, and fibers are shown below. Use bond energy values (Tables 8.4 and 8.5) to estimate ΔH for each of the reactions.

a.




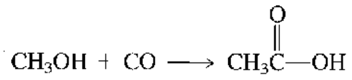
b. $4CH_2{=}CHCH_3 + 6NO \xrightarrow[Ag]{700°C} 4CH_2{=}CHCN + 6H_2O + N_2$

The nitrogen-oxygen bond energy in nitric oxide, NO, is 630 kJ/mol.

c. $2CH_2{=}CHCH_3 + 2NH_3 + 3O_2 \xrightarrow[425\text{–}510°C]{\text{Catalyst}} 2CH_2{=}CHCN + 6H_2O$

21. Is the elevated temperature noted in parts b and c of Exercise 20 needed to provide energy to endothermic reactions?

22. Acetic acid is responsible for the sour taste of vinegar. It can be manufactured using the following reaction:



$$CH_3OH + CO \longrightarrow CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Use tabulated values of bond energies (Table 8.4) to estimate ΔH for this reaction.

23. Use bond energies (Table 8.4), values of electron affinities (Table 7.7), and the ionization energy of hydrogen (1312 kJ/mol) to estimate ΔH for each of the following reactions:
a. $HF(g) \rightarrow H^+(g) + F^-(g)$
b. $HCl(g) \rightarrow H^+(g) + Cl^-(g)$
c. $HI(g) \rightarrow H^+(g) + I^-(g)$
d. $H_2O(g) \rightarrow H^+(g) + OH^-(g)$
(Electron affinity of $OH(g) = -180$ kj/mol)

Lewis Structures and Resonance

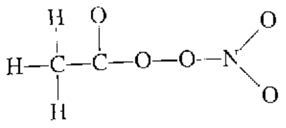
24. Write a Lewis structure for each of the following molecules and ions. In each case the first atom listed is the central atom.
a. $POCl_3$, SO_4^{2-}, XeO_4, PO_4^{3-}, ClO_4^-
b. NF_3, SO_3^{2-}, PO_3^{3-}, ClO_3^-
c. ClO_2^-, SCl_2, PCl_2^-

25. Considering your answers to Exercise 24, what conclusions can you draw concerning the structures of isoelectronic species containing the same number of atoms?

26. Write Lewis structures for the following. Show all resonance structures where applicable.
   a. NO_2^-, HNO_2, NO_3^-, HNO_3
   b. SO_4^{2-}, HSO_4^-, H_2SO_4
   c. CN^-, HCN
   d. OCN^-, SCN^-, N_3^-
   e. C_2N_2 (atomic arrangement is NCCN)

27. Some of the important pollutants in the atmosphere are ozone, sulfur dioxide, and sulfur trioxide. Write Lewis structures for these three molecules.

28. Peroxyacetylnitrate, or PAN, is a product of photochemical smog. Write Lewis structures, including resonance structures, for PAN. The skeletal arrangement of atoms is



29. Benzene (C_6H_6), consists of a six-membered ring of carbon atoms with one hydrogen bonded to each carbon. Write Lewis structures for benzene, including resonance structures.

30. An important observation supporting the need for resonance in the localized electron model was that there are only three isomers of dichlorobenzene ($C_6H_4Cl_2$). How does this fact support the need for the concept of resonance?

31. Borazine ($B_3N_3H_6$), has often been called "inorganic" benzene. Write Lewis structures for borazine. Borazine contains a six-membered ring of alternating boron and nitrogen atoms.

32. Write Lewis structures for the following molecules, which have central atoms that do not obey the octet rule: PF_5, BrF_3, $Be(CH_3)_2$, BCl_3, $XeOF_4$ (Xe is the central atom), XeF_6, SeF_4.

33. Write Lewis structures for CO_3^{2-}, HCO_3^-, and H_2CO_3. When acid is added to an aqueous solution containing carbonate or bicarbonate ions, carbon dioxide gas is formed. We generally say that carbonic acid (H_2CO_3) is unstable. Use bond energies to estimate ΔH for the reaction

$$H_2CO_3 \rightarrow CO_2 + H_2O$$

Specify a possible cause for the instability of carbonic acid.

34. Three possible Lewis structures can be written for nitrous oxide (N_2O):

$$\dot{\underset{\cdot}{N}}{=}N{=}\ddot{O}\!: \longleftrightarrow :N{\equiv}N{-}\underset{\cdot\cdot}{\ddot{O}}\!: \longleftrightarrow :\underset{\cdot\cdot}{N}{-}N{\equiv}O:$$

Given the following bond lengths,

N—N	1.67 Å	N=O	1.15 Å
N=N	1.20 Å	N—O	1.47 Å
N≡N	1.10 Å		

rationalize the observations that the N—N bond length in N_2O is 1.12 Å and that the N—O bond length is 1.19 Å.

35. Consider the following bond lengths:

C—O 1.43 Å
C=O 1.23 Å
C≡O 1.09 Å

In the CO_3^{2-} ion, all three C—O bonds have identical bond lengths of 1.36 Å. Why?

Molecular Structure and Polarity

36. Predict the molecular structure of each molecule or ion in Exercises 24 and 26.

37. Predict the molecular structure of each of the following: I_3^-, ClF_3, IF_4^+, and SF_5^+.

38. Predict the molecular structure of each of the following: SeO_3^{2-}, SeH_2, and SeO_4^{2-}.

39. Predict the molecular structures of BrF_5, KrF_4, and IF_6^+.

40. The addition of antimony pentafluoride (SbF_5) to liquid hydrogen produces a solution that is a *superacid*. Superacids are capable of acting as acids toward many compounds that we normally expect not to act as bases. For example, in the following reaction HF acts as a base:

$$SbF_5 + 2HF \rightarrow SbF_6^- + H_2F^+$$

Write Lewis structures for and predict the molecular structures of the reactants and products in this reaction.

41. Which of the following molecules have dipole moments? For the molecules that are polar, indicate the polarity of each bond and the direction of the net dipole moment of the molecule.
   a. CH_2Cl_2, $CHCl_3$, CCl_4
   b. CO_2, N_2O
   c. PH_3, NH_3, AsH_3

42. Write Lewis structures and predict the molecular structures of the following:
   a. chromate ion
   b. dichromate ion
   c. thiosulfate ion ($S_2O_3^{2-}$)
   d. peroxydisulfate ion ($S_2O_8^{2-}$)

43. What two requirements must be satisfied for a molecule to be polar?

44. Write Lewis structures and predict the molecular structures of the following:
a. OCl_2, Br_3^-, BeH_2, BH_2^-
b. BCl_3, NF_3, IF_3
c. CF_4, SeF_4, XeF_4
d. IF_5, AsF_5
Which of the above compounds have dipole moments?

45. Write a Lewis structure and predict the molecular structure and polarity of each of the following sulfur fluorides: SF_2, SF_4, SF_6, and S_2F_4 (exists as $F_3S—SF$)
Predict the F—S—F bond angles in each molecule.

Additional Exercises

46. Although both Br_3^- and I_3^- ions are known, the F_3^- ion does not exist. Explain.

47. There are three possible isomers of $PF_3(CH_3)_2$, where P is the central atom. Draw them and describe how measurements of dipole moments might be used to distinguish among them.

48. Look up the energies of the bonds in CO and N_2. Although the bond in CO is stronger, CO is considerably more reactive than N_2. Give a possible explanation.

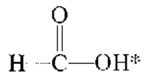
49. Carbon tetrachloride and silicon tetrachloride both exist as nonpolar liquids. When $CCl_4(l)$ is added to water, distinct layers form. When $SiCl_4(l)$ is added to water, a violent reaction occurs.

$$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$$

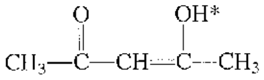
Explain why $SiCl_4$ is so much more reactive toward water than CCl_4.

50. Which of the following pairs would you expect to be more stable? Justify each choice.
a. SO_4 or SO_4^{2-}
b. NF_5 or PF_5
c. OF_6 or SF_6
d. BH_3 or BH_4^-
e. MgF or MgO
f. CsCl or $CsCl_2$
g. KBr or K_2Br

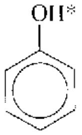
51. Many times extra stability is characteristic of a molecule or ion in which resonance is possible. How could this be used to explain the acidities of the following compounds? (The acidic hydrogen is marked by an asterisk.)

a.


$H—\overset{\overset{\displaystyle O}{\|}}{C}—OH^*$

b.


$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—CH═\overset{\overset{\displaystyle OH^*}{|}}{C}—CH_3$

c.


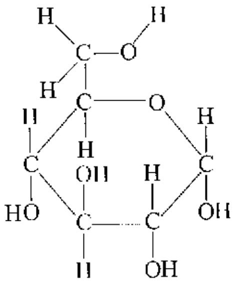
52. Would you expect the electronegativity of titanium to be the same in the species Ti, Ti^{2+}, Ti^{3+}, and Ti^{4+}? Explain your answer.

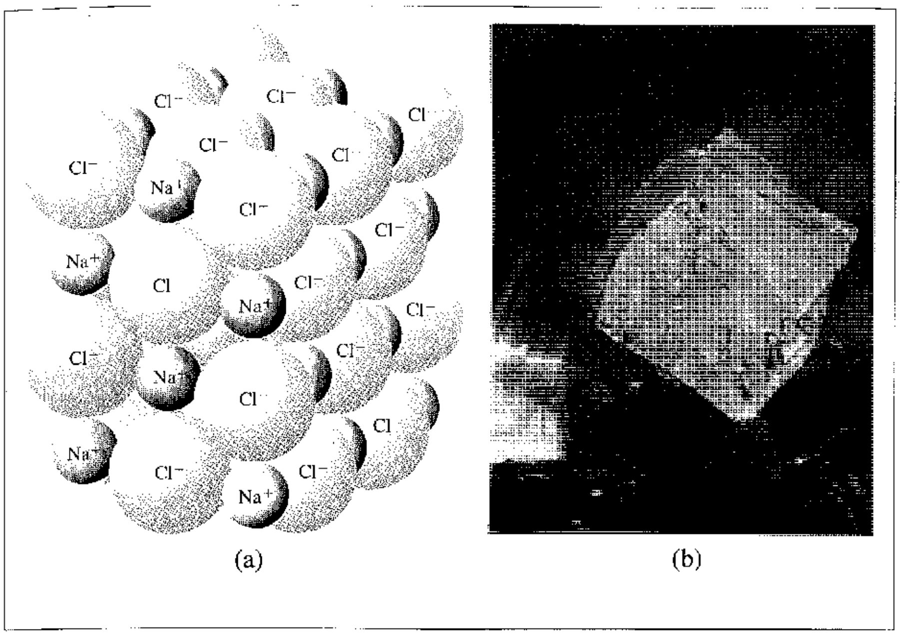
53. Write a Lewis structure and predict the molecular structure of each of the following:
a. SiF_4
b. SeF_4
c. KrF_4
Why do these three molecules have different molecular structures?

54. Write a Lewis structure and predict the molecular structure of each of the following:
a. BF_3
b. PF_3
c. BrF_3
Why are the molecular structures different? Which, if any, molecules are polar?

55. Give a rationalization for the octet rule in terms of orbitals.

56. Use bond energies (Table 8.4) to estimate ΔH for the following reactions:
a. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$
b. $C_6H_{12}O_6(s) \rightarrow 2CO_2(g) + 2C_2H_5OH(l)$
The structure of glucose, $C_6H_{12}O_6$, is:





(a)

(b)

Figure 2.19

(a) The arrangement of sodium ions (Na^+) and chloride ions (Cl^-) in the ionic compound sodium chloride.
(b) Sodium chloride (rock salt) crystals.

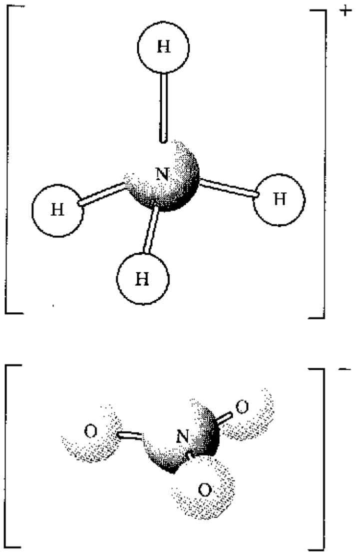


Figure 2.20

Ball-and-stick models of the ammonium ion (NH_4^+) and the nitrate ion (NO_3^-).

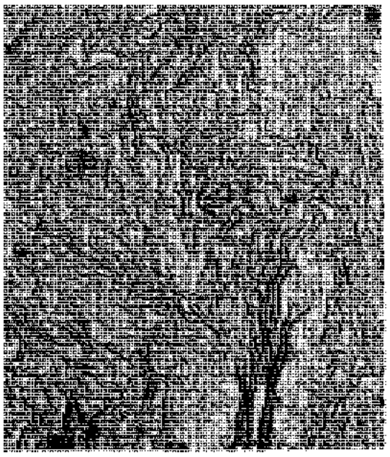
2.7 An Introduction to the Periodic Table

PURPOSE

☐ To introduce various features of the periodic table.

In a room where chemistry is taught or practiced, a chart called the **periodic table** is almost certain to be found hanging on the wall. This chart shows all of the known elements and gives a good deal of information about each. As our study of chemistry progresses, the usefulness of the periodic table will become more obvious. This section will simply introduce it to you.

A simple version of the periodic table is shown in Fig. 2.21. The letters given in the boxes are the symbols for the elements. The number shown above each symbol is the atomic number (number of protons) for that element. For example, carbon (C) has atomic number 6, and lead (Pb) has atomic number 82. Most of the elements are **metals.** Metals have characteristic physical properties such as efficient conduction of heat and electricity, malleability (they can be hammered into thin sheets), ductility (they can be pulled into wires), and (often) a lustrous appearance. Chemically, metals tend to *lose* electrons to form positive ions. For example, copper is a typical metal. It is lustrous (although it tarnishes readily); it is an excellent



Photomicrograph of gold foil.

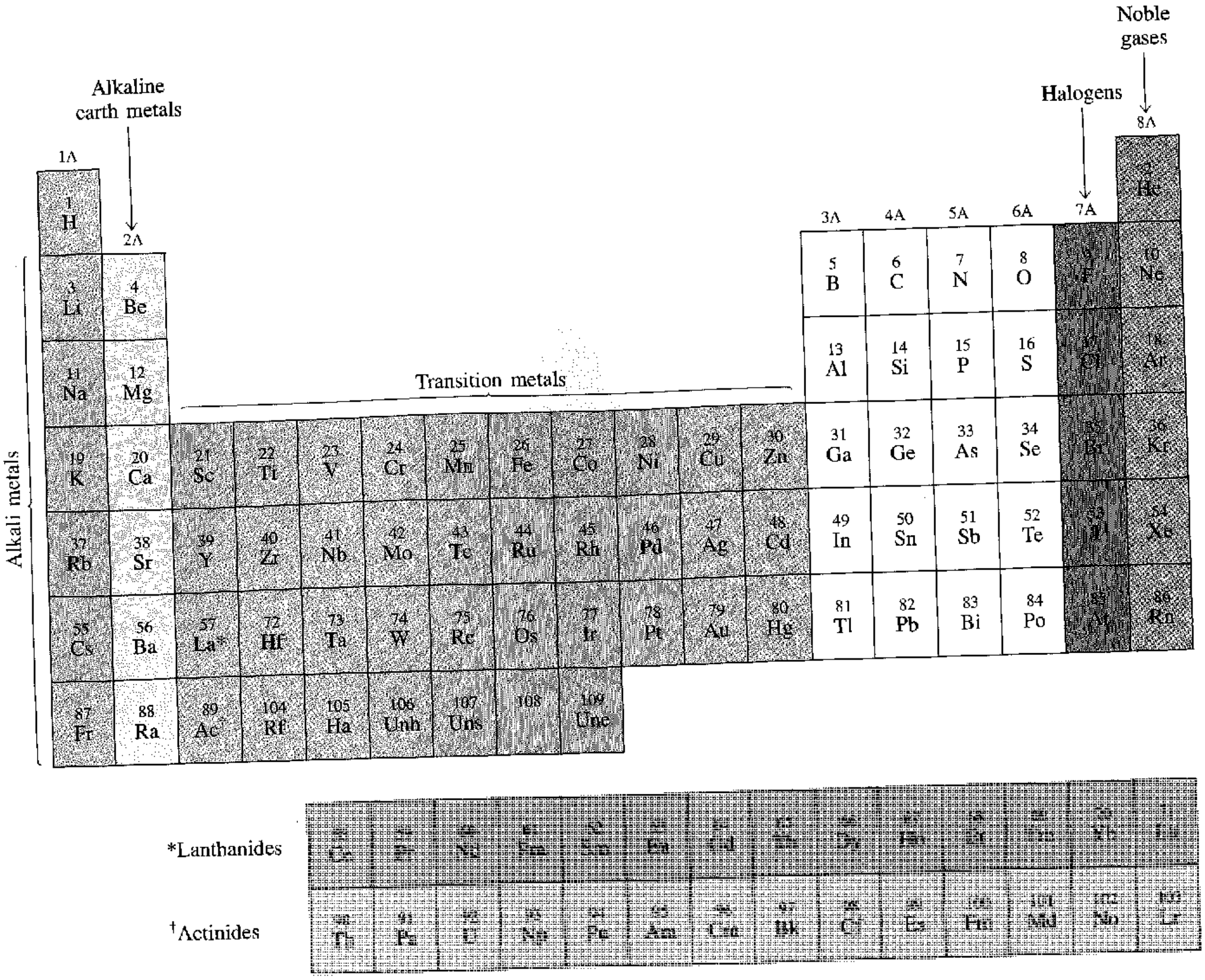


Figure 2.21

The periodic table. Although rutherfordium and hahnium have been proposed as names for elements 104 and 105, an attempt is being made to name the elements after 103 systematically, using a letter abbreviation for each number. In this system the symbol for element 104 is Unq, and for 105 is Unp. The systematic symbols are shown for elements 106, 107, and 109.

conductor of electricity (it is widely used in electrical wires); and it is readily formed into various shapes, such as pipes for water systems. Copper is also found in many salts, such as the beautifully blue copper sulfate (see page 50 for a photograph), in which copper is present as Cu^{2+} ions. Copper is a member of the transition metal family—the metals shown in the center of the periodic table.

The relatively few **nonmetals** appear in the upper right-hand corner of the table (to the right of the heavy line in Fig. 2.21), except hydrogen, a nonmetal that is grouped with the metals. The nonmetals lack the physical properties that characterize the metals. Chemically, they tend to *gain* electrons to form anions in reactions with metals. Nonmetals often bond to each other by forming covalent bonds. For example, chlorine is a typical nonmetal. Under normal conditions it exists as Cl_2 molecules; it reacts with metals to form salts containing Cl^- ions (NaCl, for example); and it forms covalent bonds with nonmetals (for example, hydrogen chloride gas, or HCl).

Metals tend to form positive ions; nonmetals tend to form negative ions.

The periodic table is arranged so that elements in the same vertical columns (called **groups**) have *similar chemical properties*. For example, all of the **alkali metals,** members of Group 1A—lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr)—are very active elements that readily form ions with a 1+ charge when they react with nonmetals. The members of Group 2A—beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra)—are called the **alkaline earth metals.** They all form ions with a 2+ charge when they react with nonmetals. The **halogens,** the members of Group 7A—fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At)—all form diatomic molecules. Fluorine, chlorine, bromine, and iodine all react with metals to form salts containing ions with a 1− charge (F^-, Cl^-, Br^-, and I^-). The members of Group 8A—helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn)—are known as the **noble gases.** They all exist under normal conditions as monatomic (single-atom) gases and have little chemical reactivity.

Elements in the same vertical column in the periodic table form a group and have similar properties.

We will learn much more about the periodic table as we continue with our study of chemistry. Meanwhile, when an element is introduced in this text, you should always note its position on the periodic table.

Another format of the periodic table will be discussed in Section 7.11.

2.8 Naming Compounds

PURPOSE

☐ To demonstrate how to name compounds given their formulas, and to write formulas given their names.

When chemistry was an infant science, there was no system for naming compounds. Names such as sugar of lead, blue vitrol, quicklime, Epsom salts, milk of magnesia, gypsum, and laughing gas were coined by early chemists. Such names are called *common names*. As chemistry grew, it became clear that using common names for compounds would lead to unacceptable chaos. More than four million chemical compounds are currently known. Memorizing common names for these compounds would be an impossible task.

The solution, of course, is to adopt a *system* for naming compounds in which the name tells something about the composition of the compound. After learning the system, a chemist given a formula should be able to name the compound, or given a name should be able to construct the compound's formula. In this section we will specify the most important rules for naming compounds other than organic compounds (those based on chains of carbon atoms).

The systematic naming of organic compounds will be discussed in Chapter 22.

We will begin with the system for naming inorganic **binary compounds**—compounds composed of two elements. The following rules apply:

1. Binary compounds are named as ionic compounds, whether or not they are, by naming the cation first and the anion second.
2. Monatomic cations take their name from the name of the element. For example, Na^+ is called sodium, Ca^{2+} is called calcium, and Al^{3+} is called aluminum in the names of compounds containing these ions.

A monatomic cation has the same name as its parent element.

3. Monatomic anions are named by taking the first part of the element name and adding *-ide*. Thus the Cl^- ion is called chloride; the F^- ion is called fluoride; the S^{2-} ion is called sulfide; and so on.

Some common monatomic cations and anions and their names are given in Table 2.2.

Common Monatomic Cations and Anions

Cation	Name	Anion	Name
H^+	hydrogen	H^-	hydride
Li^+	lithium	F^-	fluoride
Na^+	sodium	Cl^-	chloride
K^+	potassium	Br^-	bromide
Cs^+	cesium	I^-	iodide
Be^{2+}	beryllium	O^{2-}	oxide
Mg^{2+}	magnesium	S^{2-}	sulfide
Ca^{2+}	calcium	N^{3-}	nitride
Ba^{2+}	barium	P^{3-}	phosphide
Al^{3+}	aluminum		
Ag^+	silver		

Table 2.2

The rules for naming binary compounds are illustrated by the following examples:

NaCl	sodium chloride
KI	potassium iodide
CaS	calcium sulfide
Li_3N	lithium nitride
HBr	hydrogen bromide
SrSe	strontium selenide
MgO	magnesium oxide

Sample Exercise 2.3

Name each binary compound.

a. CsF **b.** $AlCl_3$ **c.** LiH

Solution

a. CsF is cesium fluoride.
b. $AlCl_3$ is aluminum chloride.
c. LiH is lithium hydride.
Notice that, in each case, the cation is named first, then the anion is named.

In many cases a pair of elements can form more than one compound. A case in point involves nitrogen and oxygen, which form the following compounds.

$$N_2O \quad NO \quad NO_2 \quad N_2O_3 \quad N_2O_4 \quad N_2O_5$$

The system that has been devised to deal with this situation for *covalent* compounds uses the Greek prefixes given in Table 2.3.

Prefixes Used to Indicate Number in Chemical Names	
Prefix	Number indicated
mono-	1
di-	2
tri-	3
tetra-	4
penta-	5
hexa-	6
hepta-	7
octa-	8

Table 2.3

For example, the nitrogen oxides are named as follows:

Compound	Systematic name	Common name
N_2O	dinitrogen monoxide	nitrous oxide
NO	nitrogen monoxide	nitric oxide
NO_2	nitrogen dioxide	
N_2O_3	dinitrogen trioxide	
N_2O_4	dinitrogen tetroxide	
N_2O_5	dinitrogen pentoxide	

Note the following additional rules for naming binary compounds:

1. The prefix *mono-* is never used for naming the first element. For example, CO is called carbon monoxide, *not* monocarbon monoxide.
2. The final *o* or *a* of the prefix is often dropped when the element begins with a vowel. For example, N_2O_4 is called dinitrogen tetroxide, *not* dinitrogen tetr*a*oxide.

Sample Exercise 2.4

Name each of the following compounds.

a. PCl_5 **b.** PCl_3 **c.** SF_6 **d.** SO_3 **e.** SO_2 **f.** CO_2

Solution

Compound	Name
a. PCl_5	phosphorus pentachloride
b. PCl_3	phosphorus trichloride
c. SF_6	sulfur hexafluoride
d. SO_3	sulfur trioxide
e. SO_2	sulfur dioxide
f. CO_2	carbon dioxide

Water and ammonia are always called by their common names.

Some compounds are always referred to by their common names. The two best examples are water and ammonia. The systematic names for H_2O and NH_3 are dihydrogen oxide and trihydrogen nitride, respectively, but these names are never used.

Do not use the covalent compound prefixes for ionic compounds.

As we will see in more detail later in the text, many metals can form more than one type of positive ion and thus more than one type of ionic compound with a given anion. For example, the compound $FeCl_2$ contains Fe^{2+} ions, and the compound $FeCl_3$ contains Fe^{3+} ions. In a case such as this, the charge on the metal ion must be specified. *Prefixes are not used for naming ionic compounds, as they are for covalent ones.* The systematic names for these two iron compounds are iron(II) chloride and iron(III) chloride, respectively, where the Roman numeral indicates the charge of the cation.

Another system for naming ionic compounds that is seen in the older literature was used for elements that form two ions. *The ion with the higher charge has a name ending in -ic, and the one with the lower charge has a name ending in -ous.* In this system, for example, Fe^{3+} is called the ferric ion, and Fe^{2+} is called the ferrous ion. The names for $FeCl_3$ and $FeCl_2$ are then ferric chloride and ferrous chloride, respectively.

Table 2.4 gives both names for many common cations. The system that uses Roman numerals will be used exclusively in this text.

Copper sulfate.

Common Names of Cations

Ion	Systematic name	Older name
Fe^{3+}	iron(III)	ferric
Fe^{2+}	iron(II)	ferrous
Cu^{2+}	copper(II)	cupric
Cu^{+}	copper(I)	cuprous
Co^{3+}	cobalt(III)	cobaltic
Co^{2+}	cobalt(II)	cobaltous
Sn^{4+}	tin(IV)	stannic
Sn^{2+}	tin(II)	stannous
Pb^{4+}	lead(IV)	plumbic
Pb^{2+}	lead(II)	plumbous
Hg^{2+}	mercury(II)	mercuric
Hg_2^{2+}*	mercury(I)	mercurous

*Note that mercury(I) ions always occur bound together to form Hg_2^{2+}.

Table 2.4

Sample Exercise 2.5

Give the systematic name of each of the following compounds.

a. CuCl **b.** HgO **c.** Fe_2O_3 **d.** MnO_2 **e.** $SnCl_4$

Solution

All these compounds include a metal that can form more than one type of cation; thus we must first determine the charge on each cation. This can be done by recognizing that a compound must be electrically neutral; that is, the positive and negative charge must exactly balance.

a. In CuCl, for example, since the anion is Cl^-, the cation must be Cu^+. The name is copper(I) chloride, where the Roman numeral I indicates the 1+ charge on Cu^+.
b. In HgO, since the anion is oxide, O^{2-}, the mercury cation must be Hg^{2+} to give a net charge of zero as required. Thus the name is mercury(II) oxide.
c. In Fe_2O_3, the three O^{2-} ions carry a total charge of 6−, and the two iron cations must carry a total charge of 6+. Thus each iron ion is Fe^{3+}, and the name is iron(III) oxide.
d. In the compound MnO_2, the cation has a 4+ charge, and the name is manganese(IV) oxide.
e. In $SnCl_4$, the cation also has a 4+ charge, so the name is tin(IV) chloride.

Note that the use of a Roman numeral in a systematic name is required only in cases where more than one ionic compound forms between a given pair of elements. This most commonly occurs for compounds containing transition metals, which often form more than one cation. *Elements that form only one cation do not need to be identified by a Roman numeral.* Common metals that do not require Roman numerals are the Group 1A elements, which form only 1+ ions; the Group 2A elements, which form only 2+ ions; and aluminum, which forms only Al^{3+}.

A compound containing a transition metal must have a Roman numeral in its name

As shown in Sample Exercise 2.5, when a metal ion is present that forms more than one type of cation, the charge on the metal ion must be determined by balancing the positive and negative charges of the compound. To do this you must be able to recognize the common cations and anions and know their charges (see Tables 2.2 and 2.5)

Sample Exercise 2.6

Give the systematic name of each of the following compounds.

a. $CoBr_2$ **b.** $CaCl_2$ **c.** Al_2O_3 **d.** P_2O_5 **e.** $CrCl_3$

Solution

Compound	Name	Comment
a. $CoBr_2$	cobalt(II) bromide	Cobalt is a transition metal; the compound name must have a Roman numeral. The two Br^- ions must be balanced by a Co^{2+} cation.
b. $CaCl_2$	calcium chloride	Calcium, an alkaline earth metal, forms only the Ca^{2+} ion. A Roman numeral is not necessary.
c. Al_2O_3	aluminum oxide	Aluminum forms only Al^{3+}. A Roman numeral is not necessary.
d. P_2O_5	diphosphorus pentoxide	This compound is formed between nonmetals. Use prefixes in the name.
e. $CrCl_3$	chromium(III) chloride	Chromium is a transition metal. The compound name must have a Roman numeral. $CrCl_3$ contains Cr^{3+}.

Names of polyatomic ions must be memorized.

A type of ionic compound that we have not yet considered is exemplified by ammonium nitrate, NH_4NO_3, which contains the polyatomic ions NH_4^+ and NO_3^-. Ammonium nitrate is classified as an ionic compound even though the NH_4^+ and NO_3^- ions contain covalent bonds, because it exhibits the properties normally associated with ionic materials. Polyatomic ions are assigned special names that you must memorize in order to name the compounds containing them. The most important polyatomic ions and their names are listed in Table 2.5.

Names of Common Polyatomic Ions

Ion	Name	Ion	Name
NH_4^+	ammonium	CO_3^{2-}	carbonate
NO_2^-	nitrite	HCO_3^-	hydrogen carbonate
NO_3^-	nitrate		(bicarbonate is a widely
SO_3^{2-}	sulfite		used common name)
SO_4^{2-}	sulfate	ClO^-	hypochlorite
HSO_4^-	hydrogen sulfate	ClO_2^-	chlorite
	(bisulfate is a widely	ClO_3^-	chlorate
	used common name)	ClO_4^-	perchlorate
OH^-	hydroxide	$C_2H_3O_2^-$	acetate
CN^-	cyanide	MnO_4^-	permanganate
PO_4^{3-}	phosphate	$Cr_2O_7^{2-}$	dichromate
HPO_4^{2-}	hydrogen phosphate	CrO_4^{2-}	chromate
$H_2PO_4^-$	dihydrogen phosphate	O_2^{2-}	peroxide

Table 2.5

Note in Table 2.5 that several series of anions contain an atom of a given element and different numbers of oxygen atoms. These anions are called **oxyanions.** When there are two members in such a series, the name of the one with the smaller number of oxygen atoms ends in *-ite* and the name of the one with the larger number ends in *-ate,* for example, sulfite (SO_3^{2-}) and sulfate (SO_4^{2-}). When more than two oxyanions make up a series, *hypo-* (less than) and *per-* (more than) are used as prefixes to name the members of the series with the fewest and the most oxygen atoms, respectively. The best example involves the oxyanions containing chlorine:

ClO^-	*hypo*chlor*ite*
ClO_2^-	chlor*ite*
ClO_3^-	chlor*ate*
ClO_4^-	*per*chlor*ate*

Sample Exercise 2.7

Give the systematic name of each of the following compounds.

a. Na_2SO_4	**b.** KH_2PO_4	**c.** $Fe(NO_3)_3$
d. $Mn(OH)_2$	**e.** Na_2SO_3	**f.** Na_2CO_3
g. $NaHCO_3$	**h.** $CsClO_4$	**i.** NaOCl
j. Na_2SeO_4	**k.** $KBrO_3$	

Solution

Compound	Name	Comment
a. Na_2SO_4	sodium sulfate	
b. KH_2PO_4	potassium dihydrogen phosphate	
c. $Fe(NO_3)_3$	iron(III) nitrate	Transition metal—name must contain a Roman numeral. Fe^{3+} ion balances three NO_3^- ions.
d. $Mn(OH)_2$	manganese(II) hydroxide	Transition metal—name must contain a Roman numeral. Mn^{2+} ion balances two OH^- ions.
e. Na_2SO_3	sodium sulfite	
f. Na_2CO_3	sodium carbonate	
g. $NaHCO_3$	sodium hydrogen carbonate	Often called sodium bicarbonate.
h. $CsClO_4$	cesium perchlorate	
i. $NaOCl$	sodium hypochlorite	
j. Na_2SeO_4	sodium selenate	Polyatomic anions of the atoms in the same group are named similarly. Thus SeO_4^{2-} is selenate, like SO_4^{2-} (sulfate).
k. $KBrO_3$	potassium bromate	As above, BrO_3^- is bromate, like ClO_3^- (chlorate).

So far we have started with the chemical formula of a compound and decided on its systematic name. The reverse process is also important. For example, given the name calcium hydroxide, we can write the formula as $Ca(OH)_2$ since we know that calcium only forms Ca^{2+} ions and that, since hydroxide is OH^-, two of these anions will be required to give a neutral compound. Similarly the name iron(II) oxide implies the formula FeO, since the Roman numeral II indicates the presence of Fe^{2+} and since the oxide ion is O^{2-}.

Sample Exercise 2.8

Given the following systematic names, write the formula for each compound.

a. ammonium sulfate **b.** vanadium(V) fluoride **c.** dioxygen difluoride
d. rubidium peroxide **e.** gallium oxide

Solution

Name	Chemical formula	Comment
a. ammonium sulfate	$(NH_4)_2SO_4$	Two ammonium ions (NH_4^+) are required for each sulfate ion (SO_4^{2-}) to achieve charge balance.
b. vanadium(V) fluoride	VF_5	The compound contains V^{5+} ions and requires five F^- ions for charge balance.
c. dioxygen difluoride	O_2F_2	The prefix di- indicates two of each atom.
d. rubidium peroxide	Rb_2O_2	Since rubidium is in group 1A, it forms only 1+ ions. Thus two Rb^- ions are needed to balance the 2− charge on the peroxide ion (O_2^{2-}).
e. gallium oxide	Ga_2O_3	Since gallium is in group 3A, like aluminum, it forms 3+ ions. Two Ga^{3+} ions are required to balance the charge on three O^{2-} ions.

Acids

When dissolved in water, certain molecules produce a solution containing free H^+ ions (protons). These substances were first recognized by the sour taste of their solutions. For example, citric acid ($H_3C_6H_5O_7$) is responsible for the tartness of lemons, limes, and oranges. Acids will be discussed in detail in Chapters 4, 14, and 15. Here we will simply present the rules for naming acids.

An acid can be viewed as a molecule with one or more H^+ ions attached to an anion. The rules for naming acids depend on whether or not the anion contains oxygen. If the *anion does not contain oxygen,* the acid is named with the prefix *hydro-* and the suffix *-ic*. For example, when gaseous HCl is dissolved in water, it forms hydrochloric acid. Similarly, HCN and H_2S dissolved in water are called hydrocyanic and hydrosulfuric acids, respectively.

When the *anion contains oxygen,* the acid name is formed from the root name of the anion with a suffix of *-ic* or *-ous*. If the anion name ends in *-ate*, the *-ate* is replaced by *-ic* (or sometimes *-ric*). For example, H_2SO_4 contains the sulfate anion (SO_4^{2-}) and is called sulfuric acid; H_3PO_4 contains the phosphate anion (PO_4^{3-}) and is called phosphoric acid; and $HC_2H_3O_2$ contains the acetate ion ($C_2H_3O_2^-$) and is called acetic acid. If the anion has an *-ite* ending, the *-ite* is replaced by *-ous*. For example, H_2SO_3, which contains sulfite (SO_3^{2-}), is named sulfurous acid; and HNO_2, which contains nitrite (NO_2^-), is named nitrous acid.

The application of these rules can be seen in the names of the acids of the oxyanions of chlorine, as shown in Table 2.6.

The names of the most important acids are given in Tables 2.7 and 2.8.

The Names of the Acids of the Oxyanions of Chlorine

Acid	Anion	Name
$HClO_4$	perchlor*ate*	perchlor*ic* acid
$HClO_3$	chlor*ate*	chlor*ic* acid
$HClO_2$	chlor*ite*	chlor*ous* acid
HClO	hypochlor*ite*	hypochlor*ous* acid

Table 2.6

Names of Acids That Do Not Contain Oxygen

Acid	Name
HF	hydrofluoric acid
HCl	hydrochloric acid
HBr	hydrobromic acid
HI	hydroiodic acid
HCN	hydrocyanic acid
H_2S	hydrosulfuric acid

Table 2.7

Names of Some Oxygen-Containing Acids

Acid	Name
HNO_3	nitric acid
HNO_2	nitrous acid
H_2SO_4	sulfuric acid
H_2SO_3	sulfurous acid
H_3PO_4	phosphoric acid
$HC_2H_3O_2$	acetic acid

Table 2.8

CHEMICAL IMPACT

BERZELIUS, SELENIUM, AND SILICON

Jöns Jakob Berzelius (Fig. 2.22) was probably the best experimental chemist of his generation and, given the crudeness of his laboratory equipment, maybe the best of all time. Unlike Lavoisier, who could afford to buy the best laboratory equipment available, Berzelius worked with minimal equipment in very plain surroundings. One of Berzelius's students described the Swedish chemist's workplace: "The laboratory consisted of two ordinary rooms with the very simplest arrangements; there were neither furnaces nor hoods, neither water system nor gas. Against the walls stood some closets with the chemicals, in the middle the mercury trough and the blast lamp table. Beside this was the sink consisting of a stone water holder with a stopcock and a pot standing under it. [Next door in the kitchen] stood a small heating furnace."

In these simple facilities Berzelius performed more than 2000 experiments over a ten-year period to determine accurate atomic masses for the 50 elements then known. His success can be seen from the data in Table 2.9. These remarkably accurate values attest to his experimental skills and patience.

Besides his table of atomic weights, Berzelius made many other major contributions to chemistry. The most important of these was the invention of a simple set of symbols for the elements along with a system for writing the formulas of compounds to replace the awkward symbolic representations of the alchemists (see Table 2.10). Although some chemists, including Dalton, objected to the new system, it was gradually adopted and forms the basis of the system we use today.

In addition to these accomplishments, Berzelius also discovered the elements cerium, thorium, selenium, and silicon. Of these elements, selenium and silicon are particularly important in today's world. Berzelius discovered selenium in 1817 in connection with his studies of sulfuric acid. For years selenium's toxicity has been known, but only recently have we become aware that it may have a positive effect on human health. Studies have shown that trace amounts of selenium in the diet may protect people from heart disease and cancer. One study based on data from 27 countries showed an inverse relationship between the cancer death rate and the selenium content of soil in a particular region (low cancer death rate in areas with high selenium content). Another research paper re-

Figure 2.22

Jöns Jakob Berzelius (1779–1848).

Comparison of Several of Berzelius's Atomic Weights with the Modern Values

Element	Atomic weight	
	Berzelius's value	Current value
Chlorine	35.41	35.45
Copper	63.00	63.55
Hydrogen	1.00	1.01
Lead	207.12	207.2
Nitrogen	14.05	14.01
Oxygen	16.00	16.00
Potassium	39.19	39.10
Silver	108.12	107.87
Sulfur	32.18	32.06

Table 2.9

CHEMICAL IMPACT

The Alchemists' Symbols for Some Common Elements and Compounds	
Substance	Alchemists' symbol
Silver	
Lead	
Tin	
Platinum	
Sulfuric acid	
Alcohol	
Sea salt	

Table 2.10

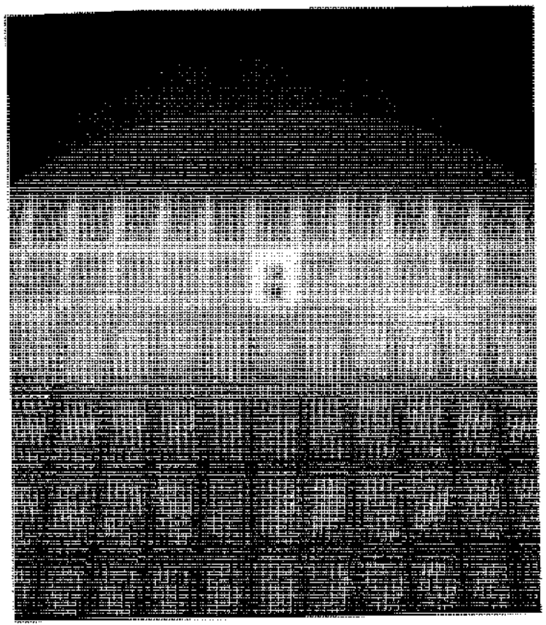


Figure 2.23
A silicon chip.

ported an inverse relationship between the selenium content of the blood and the incidence of breast cancer in women. Selenium is also found in the heart muscle and may play an important role in proper heart function. Because of these and other studies, selenium's reputation has improved, and many scientists are now studying its function in the human body.

Silicon is the second most abundant element in the earth's crust, exceeded only by oxygen. As we will see in Chapter 10, compounds involving silicon bonded to oxygen make up most of the earth's sand, rock, and soil. Berzelius prepared silicon in its pure form in 1824 by heating silicon tetrafluoride (SiF_4) with potassium metal. Today, silicon forms the basis for the modern microelectronics industry centered near San Francisco in a place that has come to be known as "Silicon Valley." The technology of the silicon chip (Fig. 2.23) with its printed circuits has transformed computers from room-sized monsters with thousands of unreliable vacuum tubes to desktop and notebook-sized units with trouble-free "solid-state" circuitry*.

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*For further reading see Bernard Jaffe, *Crucibles: The Story of Chemistry* (Premiere Book, 1957).

Summary

Three fundamental laws formed the basis for early chemistry: the law of conservation of mass (matter can neither be created nor destroyed), the law of definite proportion (a given compound always contains exactly the same proportion of elements by mass), and the law of multiple proportions (if two elements A and B form a series of compounds, the ratios of the masses of A that combine with 1 gram of B can always be represented by small whole numbers). Dalton accounted for these laws in his atomic theory. He postulated that all elements are composed of atoms; that all atoms of a given element are identical; that chemical compounds are formed when atoms combine; and that the atoms themselves are not changed in a chemical reaction, but are just reorganized.

Atoms consist of a dense nucleus containing protons and neutrons, surrounded by electrons that occupy a large volume relative to the size of the nucleus. Electrons have a relatively small mass (1/1840 of the proton mass) and a negative charge. Protons have a positive charge equal in magnitude (but opposite in sign) to that on the electron. A neutron has the same mass as a proton but no charge.

Isotopes are atoms with the same number of protons (thus constituting the same element) but different numbers of neutrons. That is, isotopes have the same atomic number but different mass numbers (total numbers of neutrons and protons).

Atoms combine to form molecules by sharing electrons to form covalent bonds. A molecule can be described by a chemical formula showing the numbers and types of atoms involved, a structural formula (showing which atoms are joined to each other), or by ball-and-stick or space-filling models that show the exact positions of the atoms in space. When an atom loses one or more electrons, it forms a positive ion called a cation. If an atom gains electrons, it becomes a negatively charged anion. The interaction of oppositely charged ions to form an ionic compound is called ionic bonding.

The periodic table arranges the elements in order of increasing atomic number, and elements having similar chemical properties fall into vertical columns, or groups. Most of the elements are metals, which tend to form cations in ionic compounds with nonmetals, which are elements that tend to form anions.

Compounds can be named systematically by a set of relatively simple rules. For compounds containing both a metal and a nonmetal, the metal is always named first, followed by a name derived from the root name of the nonmetal. For compounds containing a metal that can form more than one type of cation, a Roman numeral is used in the name to specify the charge on the metal ion. In compounds containing only nonmetals, prefixes are used to specify the relative numbers of atoms.

Key Terms

law of conservation of mass (2.2)
law of definite proportion
law of multiple proportions
atomic masses (2.3)
atomic weights
Avogadro's hypothesis
cathode ray (2.4)
electron
radioactivity
nuclear atom
nucleus
proton (2.5)
neutron
isotopes
atomic number
mass number
chemical bond (2.6)
covalent bond
molecule
chemical formula
structural formula
space-filling model
ball-and-stick model
ion
cation
anion
ionic bond
polyatomic ion
periodic table (2.7)
metal
nonmetal
group
alkali metals
alkaline earth metals
halogens
noble gases
binary compound (2.8)

Exercises

Development of the Atomic Theory

1. Several compounds containing only sulfur (S) and fluorine (F) are known. Three of them have the following compositions:

   i. 1.188 g of F for every 1.000 g of S
   ii. 2.375 g of F for every 1.000 g of S
   iii. 3.563 g of F for every 1.000 g of S

   How do these data illustrate the law of multiple proportions?

2. A reaction of 1 L of chlorine gas (Cl_2) with 3 L of fluorine gas (F_2) yields 2 L of a gaseous product. All gas volumes are at the same temperature and pressure. What is the formula of the gaseous product?

3. When mixtures of gaseous H_2 and gaseous Cl_2 react, a product forms that has the same properties regardless of the relative amounts of H_2 and Cl_2 used.

a. How is this result interpreted in terms of the law of definite proportion?

b. When a volume of H_2 reacts with an equal volume of Cl_2 at the same temperature and pressure, what volume of product having the formula HCl is formed?

4. Early tables of atomic weights were generated by measuring the mass of a substance that reacts with 1 g of oxygen. Given the following data and taking the atomic weight of hydrogen as 1.00, generate a table of relative atomic weights for these elements.

Element	Mass that combines with 1.00 g oxygen	Assumed formula
Hydrogen	0.1260 g	HO
Sodium	2.8750 g	NaO
Magnesium	1.5000 g	MgO

How do your values compare with those in the periodic table? How do you account for any differences?

5. The vitamin niacin (nicotinic acid, $C_6H_5NO_2$) can be isolated from a variety of natural sources; for example, liver, yeast, milk, and whole grain. It can also be synthesized from commercially available materials. Which source of nicotinic acid, from a nutritional view, is best for use in a multivitamin tablet? Why?

6. How does Dalton's atomic theory account for each of the following?

a. the law of conservation of mass
b. the law of definite proportion
c. the law of multiple proportions

7. What refinements had to be made in Dalton's atomic theory to account for Guy-Lussac's results on the combining volumes of gases?

8. One of the best indications of a "good" theory is that it raises more questions for further experimentation than it originally answered. Does this apply to Dalton's atomic theory? If so, in what ways?

The Nature of the Atom

9. What evidence led to the conclusion that cathode rays had a negative charge?

10. Is there a difference between a cathode ray and a β particle?

11. From the information in this chapter on the mass of the proton, the mass of the electron, and the sizes of the nucleus and the atom, calculate the densities of a hydrogen nucleus and a hydrogen atom.

12. A chemist in a galaxy far, far away performed the Millikan oil drop experiment and got the following results for the charge on various drops. What is the charge of the electron in zirkombs?

2.56×10^{-12} zirkombs	7.68×10^{-12} zirkombs
3.84×10^{-12} zirkombs	5.12×10^{-12} zirkombs

Elements and the Periodic Table

13. What is the distinction between atomic number and mass number? Between mass number and atomic weight?

14. Give the number of protons and neutrons in the nucleus of each of the following atoms:

a. $^{238}_{94}Pu$ c. $^{52}_{24}Cr$
b. $^{65}_{29}Cu$ d. $^{4}_{2}He$

15. Using the periodic table, give the number of protons and neutrons in the nucleus of each of the following atoms:

a. ^{15}N c. ^{207}Pb e. ^{107}Ag
b. ^{3}H d. ^{151}Eu

16. Identify each of the following elements:

a. $^{31}_{15}X$ c. $^{39}_{19}X$
b. $^{127}_{53}X$ d. $^{173}_{70}X$

17. How many protons, neutrons, and electrons are in each of the following atoms or ions?

a. $^{24}_{12}Mg$ d. $^{59}_{27}Co^{3+}$ g. $^{79}_{34}Se^{2-}$
b. $^{24}_{12}Mg^{2+}$ e. $^{59}_{27}Co$
c. $^{59}_{27}Co^{2+}$ f. $^{79}_{34}Se$

18. An ion contains 50 protons, 68 neutrons, and 48 electrons. What is its symbol?

19. Complete the following table:

Symbol	Number of protons in nucleus	Number of neutrons in nucleus	Number of electrons	Net change
	33	42		3+
$^{128}_{52}Te^{2-}$			54	
	16	16	16	
	81	123		1+
$^{195}_{78}Pt$				

20. Classify the following elements as metals or nonmetals: Mg, Ti, Au, Bi, Si, Ge, B, At, Rn, Eu, Am, Br.

21. The distinction between metals and nonmetals is really not a clear one. Some elements, called *metalloids*, are intermediate in their properties. Which elements in Exercise 20 would you reclassify as metalloids? What other elements in the periodic table would you expect to be metalloids?

22. Which of the following sets of elements are all in the same group in the periodic table?
   a. Fe, Ru, Os
   b. Rh, Pd, Ag
   c. Sn, As, S
   d. Se, Te, Po
   e. N, P, O
   f. C, Si, Ge
   g. Rb, Sn
   h. Mg, Ca

23. Would you expect each of the following atoms to gain or lose electrons when forming ions? What is the most likely ion each will form?
   a. Na
   b. Sr
   c. Ba
   d. I
   e. Al
   f. S

Nomenclature

24. Name the following compounds:
   a. CrO_3
   b. Cr_2O_3
   c. Al_2O_3
   d. SeO_2
   e. SeO_3
   f. NI_3
   g. PCl_3

25. Name the following compounds:
   a. NiO
   b. Fe_2O_3
   c. CeO_2
   d. Ce_2O_3
   e. Ag_2S
   f. MnO_2
   g. NaH
   h. H_2S

26. Name the following compounds:
   a. $NaCl$
   b. $MgCl_2$
   c. $RbBr$
   d. CsF
   e. AlI_3
   f. HI
   g. NO
   h. NF_3
   i. N_2F_4
   j. N_2Cl_2

27. Name the following compounds:
   a. $KClO_4$
   b. $Ca_3(PO_4)_2$
   c. $Al_2(SO_4)_3$
   d. $Pb(NO_3)_2$
   e. $BaSO_3$
   f. $NaNO_2$
   g. $KMnO_4$
   h. $K_2Cr_2O_7$
   i. $AuCl_3$
   j. HIO_2

28. Name the following compounds:
   a. HNO_3
   b. HNO_2
   c. H_3PO_4
   d. H_3PO_3
   e. $NaHSO_4$
   f. $Ca(HSO_3)_2$
   g. $NaBrO_3$
   h. $Fe(IO_4)_3$
   i. $Ru(NO_3)_3$
   j. V_2O_5

29. Write formulas for the following compounds:
   a. cesium bromide
   b. barium sulfate
   c. ammonium chloride
   d. chlorine monoxide

30. Write formulas for the following compounds:
   a. ammonium hydrogen phosphate
   b. mercury(I) sulfide
   c. silicon dioxide
   d. sodium sulfite
   e. aluminum hydrogen sulfate
   f. nitrogen trichloride
   g. hydrobromic acid
   h. bromous acid
   i. perbromic acid

31. Write formulas for the following compounds:
   a. sulfur difluoride
   b. sulfur hexafluoride
   c. sodium dihydrogen phosphate
   d. lithium nitride
   e. chromium(III) carbonate
   f. tin(II) fluoride

32. Write formulas for the following compounds:
   a. sodium hydroxide
   b. aluminum hydroxide
   c. hydrogen cyanide
   d. sodium peroxide
   e. copper(II) acetate
   f. carbon tetrafluoride

Additional Exercises

33. Insulin is a complex protein molecule produced by the pancreas in all vertebrates. It is a hormone that regulates carbohydrate metabolism. Inability to produce insulin results in diabetes mellitus. Diabetes is treated by prescribing injections of insulin. Given the law of definite proportion, would you expect any differences in chemical activity between human insulin extracted from pancreatic tissue and human insulin produced by genetically engineered bacteria? Why or why not?

34. Technetium (Tc) was the first synthetically produced element. Technetium comes from the Greek word for "artificial." It was first produced by Perries and Segré in 1937 in Berkeley, California, by bombarding a molybdenum plate with ^{2}H nuclei. Elemental technetium is produced from ammonium pertechnetate. How many protons and neutrons are in the nuclei of ^{98}Tc and ^{99}Tc? What is the formula of ammonium pertechnetate?

35. The early alchemists used to do an experiment in which water was boiled for several days in a sealed glass container. Eventually, some solid residue would begin to appear in the bottom of the flask. This result was interpreted to mean that some of the water in the flask had been converted into earth. When Lavoisier repeated this experiment, he found that the water weighed the same before and after heating, and the weight of the flask plus the solid residue equaled the original weight of the flask. Were the alchemists correct? Explain what really happened. (This experiment is described in the article by A. F. Scott, in *Scientific American*, January 1984.)

36. What results would you predict from the Rutherford α-particle scattering experiment if the plum pudding model of the atom were correct?