**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 H₂ 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.

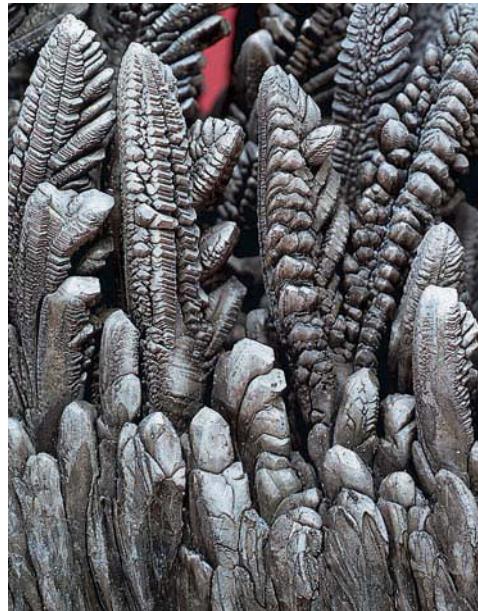
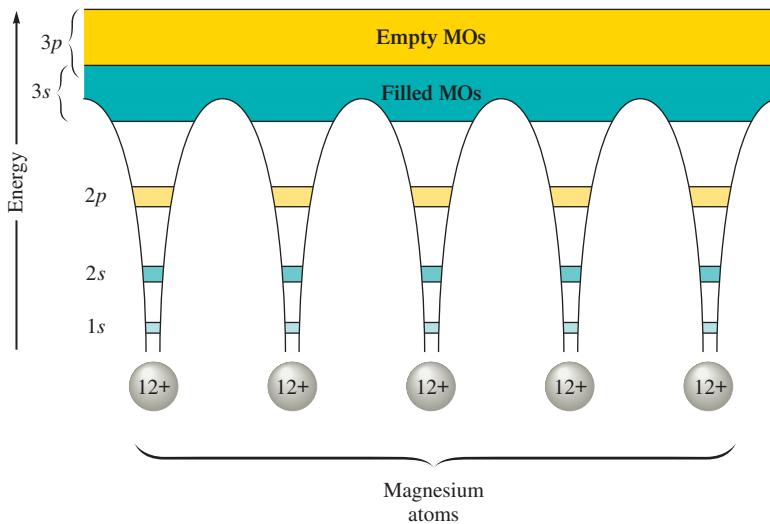
as in a metal crystal, the large number of resulting molecular orbitals become more closely spaced and finally form a virtual continuum of levels, called *bands*, as shown in Fig. 10.19.

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 electric potential is placed across a strip of metal, for current to flow, electrons must be free to move. In the band model for metals, the electrons in partially filled bonds are mobile. 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.

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.

**FIGURE 10.20**

(left) A representation of the energy levels (bands) in a magnesium crystal. The electrons in the 1s, 2s, and 2p orbitals are close to the nuclei and thus are localized on each magnesium atom as shown. However, the 3s and 3p valence orbitals overlap and mix to form molecular orbitals. Electrons in these energy levels can travel throughout the crystal. (right) Crystals of magnesium grown from a vapor.



CHEMICAL IMPACT

What Sank the Titanic?

Ton April 12, 1912, the steamship *Titanic* struck an iceberg in the North Atlantic approximately 100 miles south of the Grand Banks of Newfoundland and within 3 hours was resting on the bottom of the ocean. Of her more than 2300 passengers and crew, over 1500 lost their lives. While the tragic story of the *Titanic* has never faded from the minds and imaginations of the generations that followed, the 1985 discovery of the wreck by a joint Franco-American expedition at a depth of 12,612 feet rekindled the world's interest in the "greatest oceangoing vessel" ever built. The discovery also would reveal important scientific clues as to why and how the *Titanic* sank so quickly in the frigid waters of the North Atlantic.

The *Titanic* was designed to be virtually "unsinkable," and even in the worst-case scenario, a head-on collision with another ocean liner, the ship was engineered to take from one to three days to sink. Thus its quick trip to the bottom has puzzled scientists for years. In 1991, Steve Blasco, an ocean-floor geologist for the Canadian Department of Natural Resources, led a scientific expedition to the wreck. On one of 17 dives to the site, Blasco's team recovered a piece of steel that appeared to be a part of the *Titanic*'s hull. Unlike modern steel, which would have shown evidence of bending in a collision, the steel recovered from the *Titanic* appeared to have shattered on impact with the iceberg. This suggested that the metal might not have been as ductile (*ductility* is the ability to stretch without breaking) as it should have been. In 1994, tests were conducted on small pieces of metal, called *coupons*, cut from the recovered piece of hull. These samples shattered without bending. Further analysis showed that the steel used to construct the hull of the *Titanic* was high in sulfur content, and it is known that sulfur

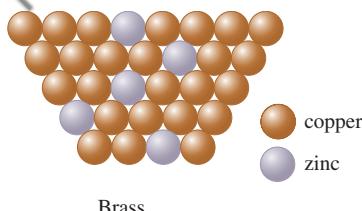
occlusions tend to make steel more brittle. This evidence suggests that the quality of the steel used to make the hull of the *Titanic* may very well have been an important factor that led to the rapid sinking of the ship.

But—not so fast. The *Titanic* continues to provoke controversy. A team of naval engineers and scientists recently have concluded that it was not brittle steel but faulty rivets that doomed the *Titanic*. During expeditions in 1996 and 1998 conducted by RMS *Titanic*, Inc., more samples of *Titanic*'s steel and rivets were obtained for further study. Analysis of these samples by a team headed by Tim Foecke of the National Institute of Standards and Technology (NIST) shows that the rivets contain three times the expected amount of silicate slag. Foecke and his colleagues argue that the high slag content resulted in weak rivets that snapped in large numbers when the collision occurred, mortally wounding the ship.

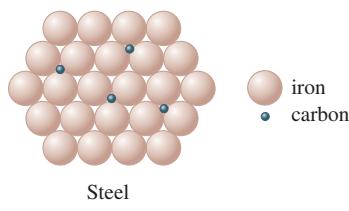
What sank the *Titanic*? It hit an iceberg. The details remain to be figured out.



Bow of the *Titanic* under $2\frac{1}{2}$ miles of water.

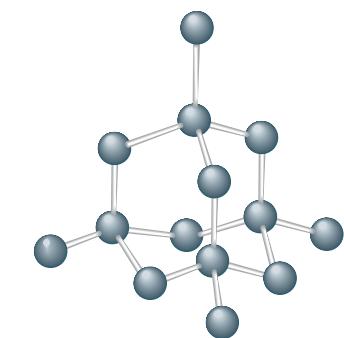
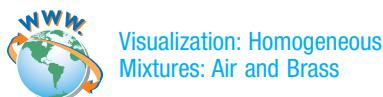


(a)

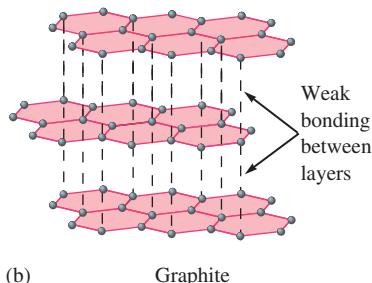


(b)

FIGURE 10.21
Two types of alloys.



(a)



(b)

FIGURE 10.22
The structures of diamond and graphite. In each case only a small part of the entire structure is shown.

TABLE 10.4 The Composition of the Two Brands of Steel Tubing 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

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 (95% tin and 5% antimony) 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 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 are used for nails, cables, and chains. *Medium steels*, containing 0.2 to 0.6% carbon, are harder than mild steels and are used in rails and structural steel beams. *High-carbon steels*, containing 0.6 to 1.5% carbon, are tough and hard and are used for springs, tools, and cutlery.

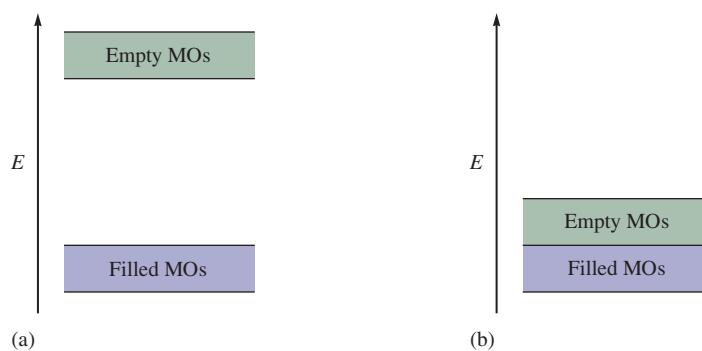
Many types of steel also contain elements in addition to iron and carbon. Such steels are often called *alloy steels*, and they can be viewed as being mixed interstitial (carbon) and substitutional (other metals) alloys. Bicycle frames, for example, are constructed from a wide variety of alloy steels. The compositions of the two brands of steel tubing most commonly used in expensive racing bicycles are given in Table 10.4.

10.5 Carbon and Silicon: Network Atomic Solids

Many atomic solids contain strong directional covalent bonds to form a solid that might best be viewed as a “giant molecule.” We 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.

The two most common forms of carbon, diamond and graphite, are typical network solids. In diamond, the hardest naturally occurring substance, each carbon atom is surrounded by a tetrahedral arrangement of other carbon atoms to form a huge molecule [see 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

**FIGURE 10.23**

Partial representation of the molecular orbital energies in (a) diamond and (b) a typical metal.



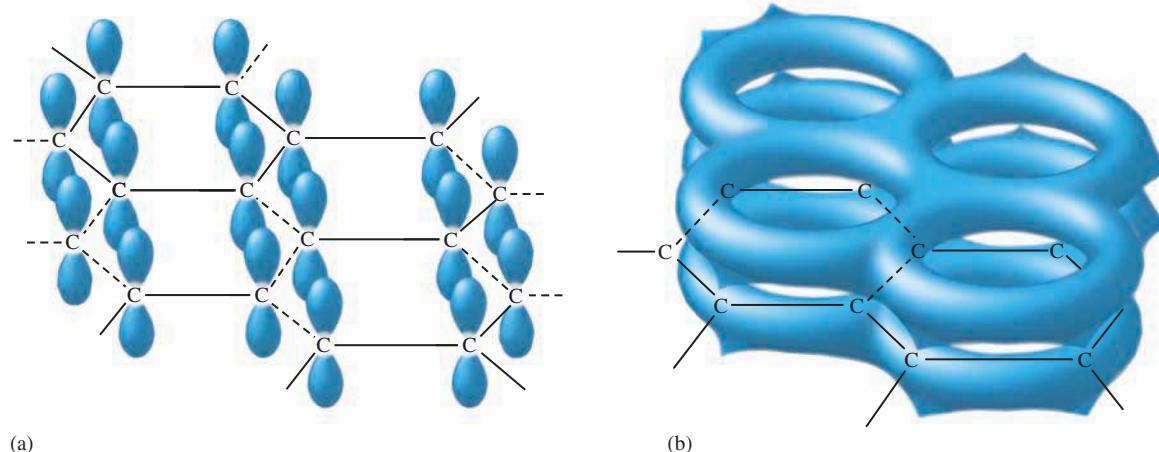
Visualization: Network Solids



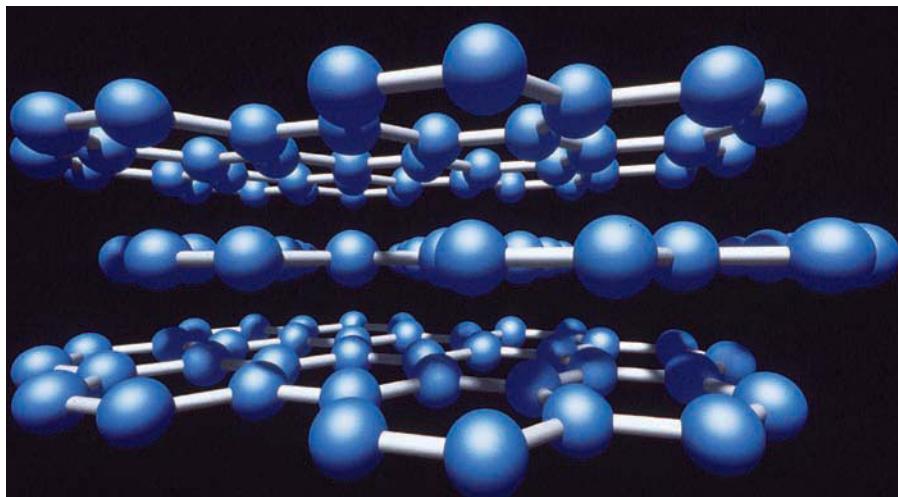
Graphite and diamond, two forms of carbon.

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 transferred easily 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 electric current.

Graphite 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 the three other carbon atoms in a trigonal planar arrangement with 120-degree 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 with 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.

**FIGURE 10.24**

The p orbitals (a) perpendicular to the plane of the carbon ring system in graphite can combine to form (b) an extensive π -bonding network.

**FIGURE 10.25**

Graphite consists of layers of carbon atoms.

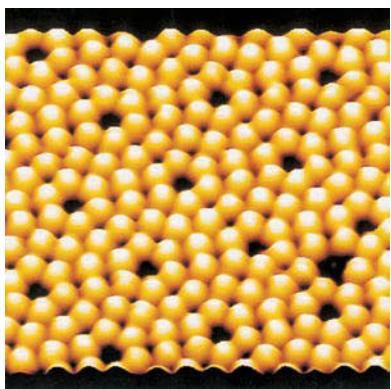
These orbitals combine to form a group of closely spaced π molecular orbitals that are important in two ways. First, they contribute significantly to the stability of the graphite layers because of the π bond formation. Second, the π molecular orbitals with their delocalized electrons account for the electrical conductivity of graphite. These closely spaced orbitals are exactly analogous to the conduction bands found in metal crystals.

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 shown in 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 used extensively 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 with 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, whereas the most stable silicon compounds involve chains with silicon–oxygen bonds.

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.



Computer-generated model of silica.

The bonding in the CO_2 molecule was described in Section 9.1.

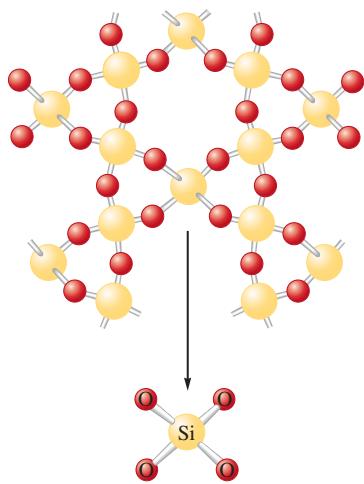
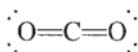


FIGURE 10.26
(top) The structure of quartz (empirical formula SiO_2). Quartz contains chains of SiO_4 tetrahedra (bottom) that share oxygen atoms.

Recall that the Lewis structure of CO_2 is



and that each $\text{C}=\text{O}$ bond can be viewed as a combination of a σ bond involving a carbon sp hybrid orbital and a π bond involving a carbon $2p$ orbital. On the contrary, silicon cannot use its valence $3p$ orbitals to form strong π bonds with 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 with 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 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.

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

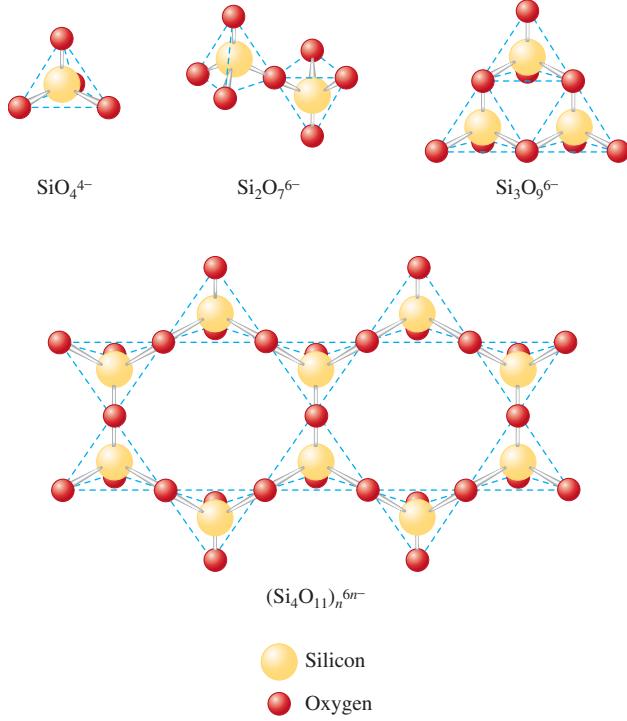


FIGURE 10.27
Examples of silicate anions, all of which are based on SiO_4^{4-} tetrahedra.

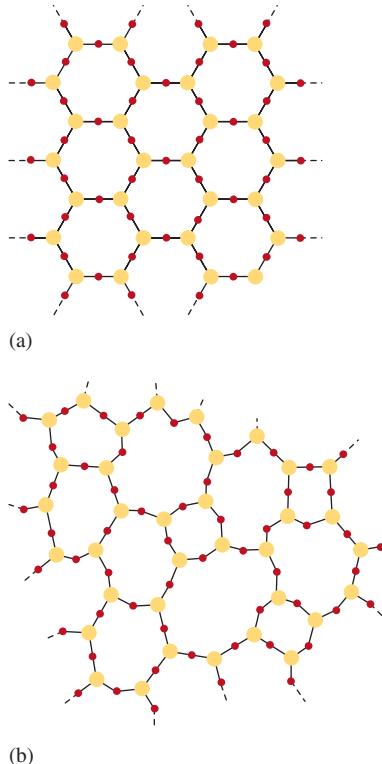


FIGURE 10.28
Two-dimensional representations of (a) a quartz crystal and (b) a quartz glass.

TABLE 10.5 Compositions of Some Common Types of Glass

<i>Type of Glass</i>	Percentages of Various Components						
	<i>SiO₂</i>	<i>CaO</i>	<i>Na₂O</i>	<i>B₂O₃</i>	<i>Al₂O₃</i>	<i>K₂O</i>	<i>MgO</i>
Window (soda-lime glass)	72	11	13	—	0.3	3.8	—
Cookware (aluminosilicate glass)	55	15	—	—	20	—	10
Heat-resistant (borosilicate glass)	76	3	5	13	2	0.5	—
Optical	69	12	6	0.3	—	12	—



A glass pitcher being manufactured.

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 10.5.

Ceramics

Ceramics are typically made from clays (which contain silicates) and hardened by firing at high temperatures. Ceramics are 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 that 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 $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$. 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 $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. 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.



An artist paints a ceramic vase before glazing.



CHEMICAL IMPACT

Golfing with Glass

You probably can guess what material traditionally was used to construct the “woods” used in golf. Modern technology has changed things. Like the bats used in college baseball, most “woods” are now made of metal. While bats are made of aluminum, golf club heads are often made of stainless steel or titanium.

Metals and their alloys usually form crystals that contain highly ordered arrangements of atoms. However, a company called Liquidmetal Golf of Laguna Niguel, California, has begun producing golf clubs containing glass—metallic glass. The company has found that when molten mixtures of titanium, zirconium, nickel, beryllium, and copper are cooled, they solidify, forming a glass. Unlike crystalline materials that contain a regular array of atoms, glasses are amorphous—the atoms are randomly scattered throughout the solid.

These golf clubs with metallic glass inserts have some unusual characteristics. Golfers who have tried the clubs say they combine hardness with a “soft feel.” Studies show that the glass transfers more of the energy of the golf swing to the ball with less impact to the golfer’s hands than with regular metal woods.

One of the fortunate properties of this five-component metallic glass (invented in 1992 by William L. Johnson and Atakan Peker at the California Institute of Technology) is that it can be cooled relatively slowly to form the glass. This allows manufacture of relatively large glass objects such as inserts for golf club heads. Most mixtures of metals that form glasses must be cooled very rapidly to obtain the glass, which results in tiny particles of glass leading to powders.



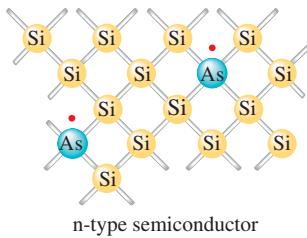
Golf clubs with a titanium shell and metallic glass inserts.

David S. Lee, head of manufacturing at Liquidmetal Golf, says that golf clubs were an obvious first application for this five-component glass because golfers are used to paying high prices for clubs that employ new technology. Liquidmetal Golf is now looking for other applications of this new glass. How about glass bicycle frames?

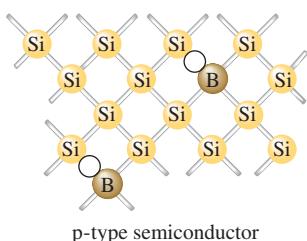
Although ceramics have been known since antiquity, they are not obsolete materials. On the contrary, ceramics constitute one of the most important classes of “high-tech” materials. Because of their stability at high temperatures and resistance to corrosion, ceramics seem an obvious choice for constructing jet and automobile engines in which the greatest fuel efficiencies are possible at very high temperatures. But ceramics are brittle—they break rather than bend—which limits their usefulness. However, more flexible ceramics can be obtained by adding small amounts of organic polymers. Taking their cue from natural “organoceramics” such as teeth and shells of sea creatures that contain small amounts of organic polymers, materials scientists have found that incorporating tiny amounts of long organic molecules into ceramics as they form produces materials that are much less subject to fracture. These materials should be useful for lighter, more durable engine parts, as well as for flexible superconducting wire and microelectronic devices. In addition, these organoceramics hold great promise for prosthetic devices such as artificial bones.



Visualization: Magnetic Levitation by a Superconductor



(a)



(b)

FIGURE 10.29

(a) A silicon crystal doped with arsenic, which has one more valence electron than silicon. (b) A silicon crystal doped with boron, which has one less electron than silicon.

Electrons must be in singly occupied molecular orbitals to conduct a current.

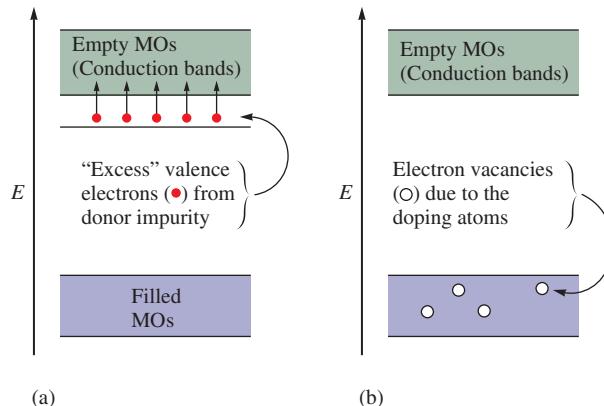
Semiconductors

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 (see Fig. 10.23). This gap prevents excitation of electrons to the empty molecular 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.

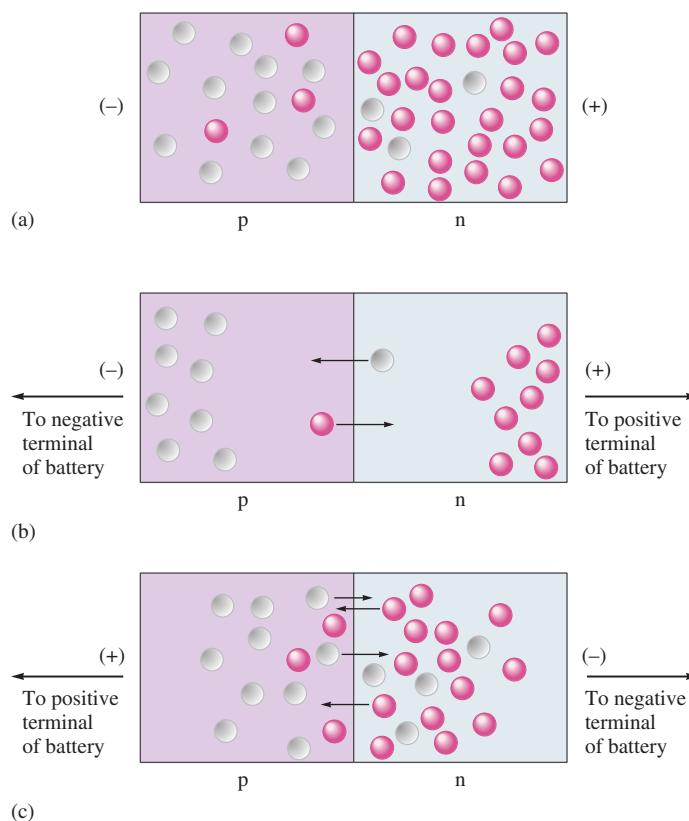
The small conductivity of silicon can be enhanced at normal temperatures if the silicon crystal is *doped* with certain other elements. For example, when a small fraction of silicon atoms is replaced by arsenic atoms, each having *one more* valence electron than silicon, extra electrons become available 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 be easily excited into these levels, where they can conduct an electric current [see Fig. 10.30(a)].

We also can 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 with 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 that there is only one electron in some of the molecular orbitals, 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 red dots

**FIGURE 10.30**

Energy-level diagrams for (a) an n-type semiconductor and (b) a p-type semiconductor.

**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 (●). (b) No current flows (reverse bias). (c) 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.

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 buildup, called the *contact potential*, or *junction potential*, prevents further migration of electrons.

Now suppose an external electric 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.

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 a pulsating direct current (flows in one direction) from 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 direct current. Radios, computers, and other electronic devices formerly



CHEMICAL IMPACT

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 handheld calculator run by a small battery now 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. 10.32. 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 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 or 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, which has replaced the large vacuum tube, 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 chip less than 1 cm wide can contain hundreds of printed circuits and be used in computers, radios, and televisions.

A printed circuit has many n–p–n junction transistors. Fig. 10.33 illustrates the formation of one transistor area. The chip begins as a thin wafer of silicon that has been doped with an n-type impurity. A protective layer of silicon dioxide 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 polymeric photoresist, as shown in Fig. 10.33(a). A template that only allows light to shine through in selected areas is then placed on top [Fig. 10.33(b)], and light is shown on the chip. The photoresist

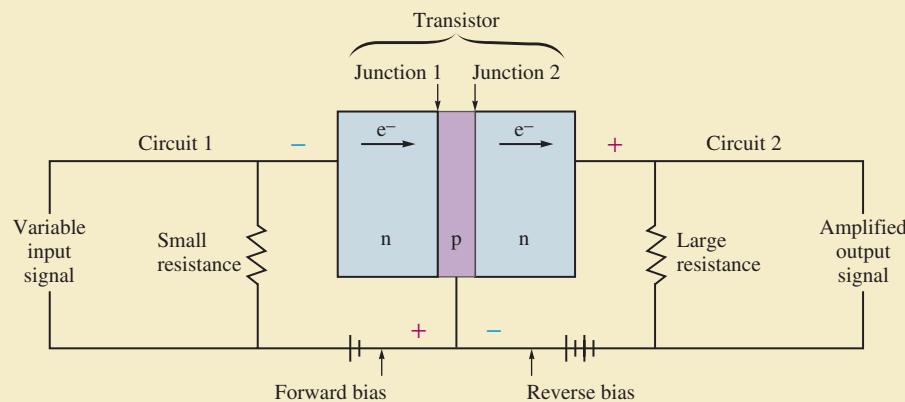


FIGURE 10.32

A schematic of two circuits connected by a transistor. The signal in circuit 1 is amplified in circuit 2.

that has been exposed to light undergoes a chemical change that causes its solubility to be different from the unexposed photoresist. The exposed photoresist is dissolved using selective solvents [Fig. 10.33(c)], and the exposed area is treated with an etching solution to dissolve the oxide coating [Fig. 10.33(d)]. When the remaining photoresist is dissolved, the silicon wafer has its oxide coating intact except at the one spot (of diameter x), as shown in Fig. 10.33(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. 10.33(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 photoresist covering is applied, which is illuminated through a template with a transparent area indicated by y [Fig. 10.33(f)]. The photoresist 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. 10.33(g). Next, conductors are layered onto the chip giving the finished transistor [Fig. 10.33(h)], which has two circuits connected through an n–p–n junction (see Fig. 10.32). This transistor then becomes a part of a large 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.

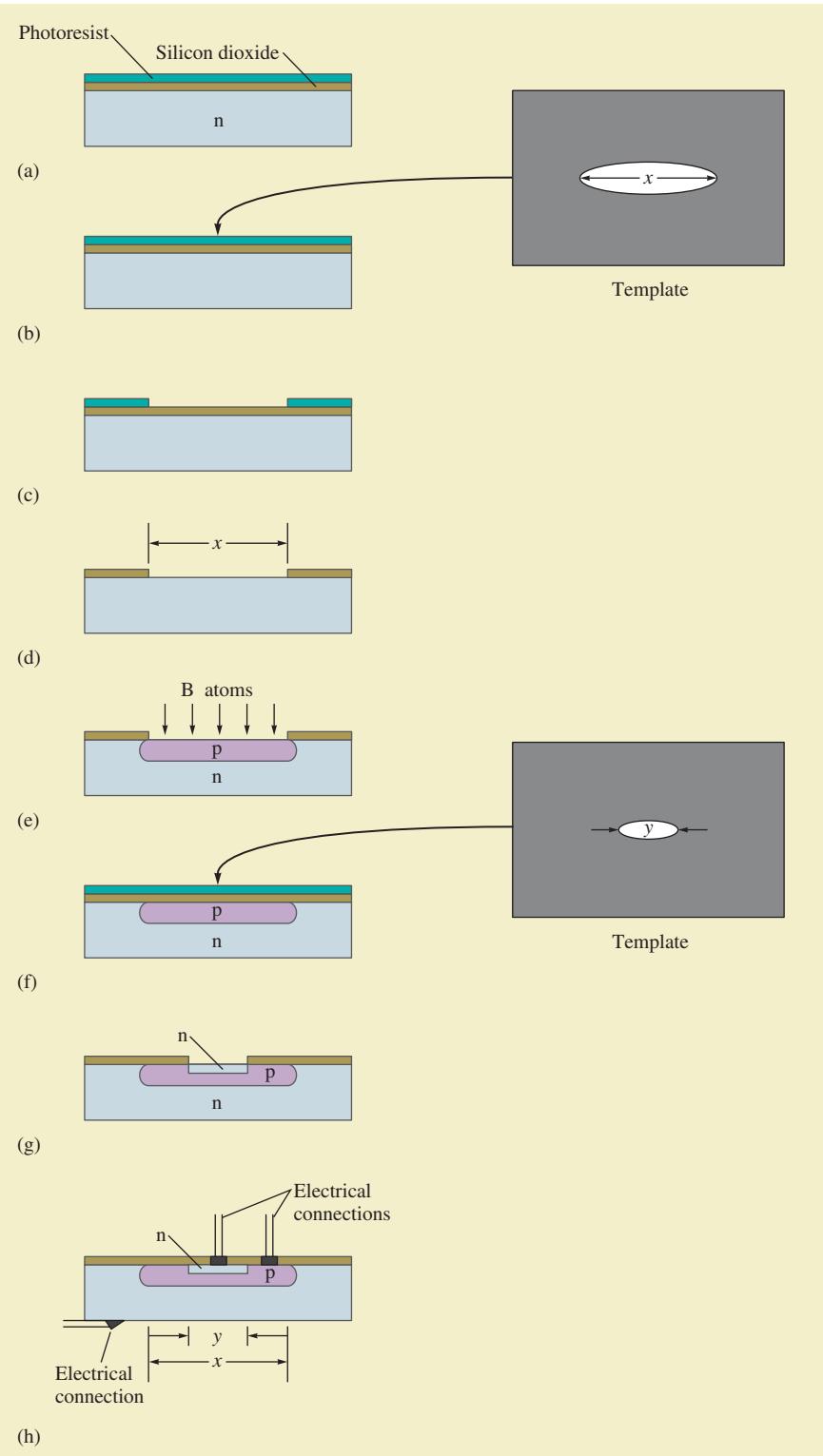


FIGURE 10.33

The steps for forming a transistor in a crystal of initially pure silicon.

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.

10.6 Molecular Solids

So far we have considered solids in which atoms occupy the lattice positions. In some of these substances (network solids), the solid can be considered to be one giant molecule. In addition, there are many types of solids that contain discrete molecular units at each lattice position. A 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. 10.34(a)], and certain forms of phosphorus that contain P_4 molecules [Fig. 10.34(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 1 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 solids shown in Table 10.6.

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 London dispersion forces. Because these forces are often relatively small, we might expect all 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 quite large, 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



A “steaming” piece of dry ice.



Visualization: Molecular Solids

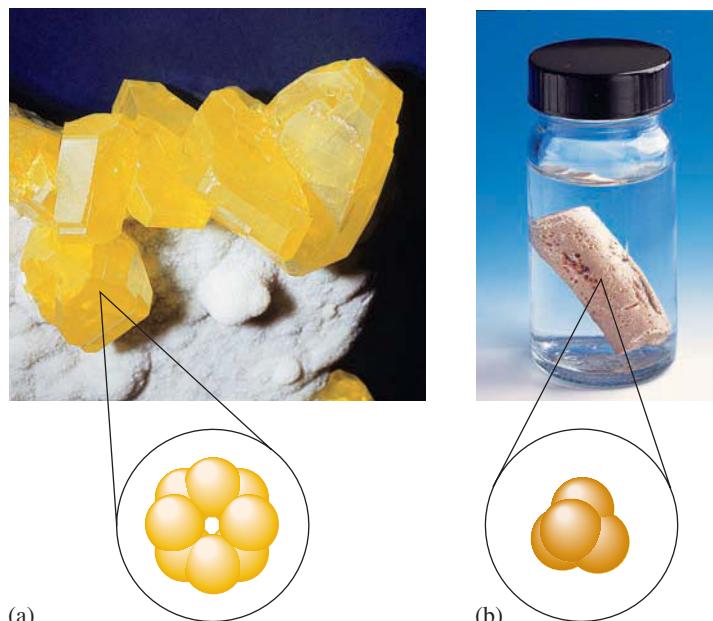


FIGURE 10.34

(a) Sulfur crystals (yellow) contain S_8 molecules. (b) White phosphorus (containing P_4 molecules) is so reactive with the oxygen in air that it must be stored under water.



CHEMICAL IMPACT

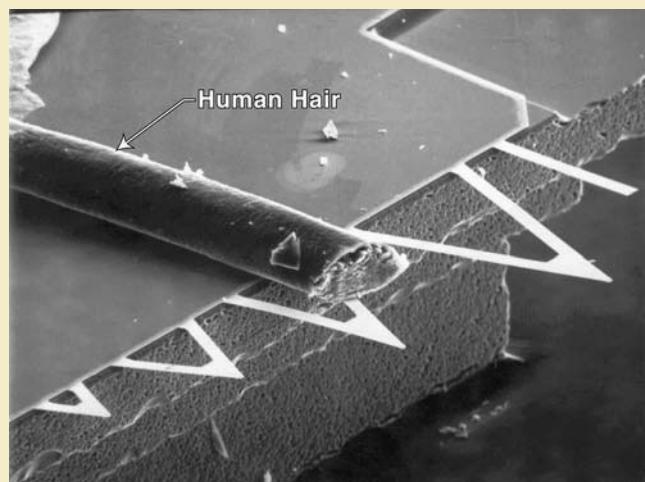
Explosive Sniffer

These days security is at the top of everyone's list of important concerns, especially for those people who are responsible for the safety of our transportation systems. In particular, airports need speedy and sensitive detectors for explosives. Plastic explosives are especially tricky to detect because they do not respond to metal detectors, and they can be shaped into innocent-looking objects to avoid X-ray detection. However, a team of scientists at Oak Ridge National Laboratory led by Thomas Thundat has just published a description of an inexpensive device that is extremely sensitive to two N-containing compounds found in plastic explosives. The key part of this detection device is a tiny (180-micrometer), V-shaped cantilever made of silicon. The cantilever is shown in the accompanying photo next to a human hair for size comparison.

The upper surface of the cantilever was first coated with a layer of gold and then a one-molecule-thick layer of an acid that binds to each of the two N-containing molecules to be detected: pentaerythritol tetranitrate (PETN) and hexahydro-1,3,5-triazine (RDX). When a stream of air containing tiny amounts of PETN or RDX passes over the cantilever, these molecules bind to the cantilever, causing it to bend "like a diving board." This bending is not due to the added mass of the attached PETN and RDX. Rather, the deformation occurs because the area of the cantilever surface where binding takes place stretches relative to the unbound areas. A laser pointed at the cantilever detects the bending motion when PETN or RDX (or both) is present. The device's sensitivity is quite remarkable: 14 parts per trillion of PETN and 30 parts per trillion of RDX.

All in all, this device appears very promising for detecting plastic explosives in luggage. The cantilevers are inexpensive to construct (approximately \$1), and the entire device is about the size of a shoe box. Also, the Oak Ridge team can fabricate thousands of cantilevers in one device. By putting different coatings on the cantilever arms, it should be possible to detect many other types of chemicals and possible biological agents.

This detector looks like a very promising addition to our arsenal of security devices.



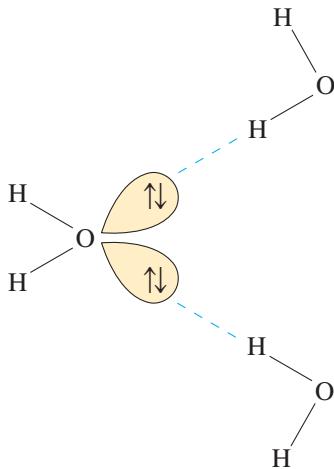
When explosive compounds bind to these V-shaped cantilevers, the microscopic structures, which are about the width of a hair, bend and produce a signal.

TABLE 10.6 Comparison of Atomic Separations Within Molecules (Covalent Bonds) and Between Molecules (Intermolecular Interactions)

Solid	Distance Between Atoms in Molecule*	Closest Distance Between Molecules in the Solid
P ₄	220 pm	380 pm
S ₈	206 pm	370 pm
Cl ₂	199 pm	360 pm

*The shorter distances within the molecules indicate stronger bonding.

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

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 closest packed anions. The packing is done in a way that maximizes the electrostatic attractions among oppositely charged ions and minimizes the repulsions among ions with like charges.

There are three types of holes in closest packed structures:

1. Trigonal holes are formed by three spheres in the same layer [Fig. 10.35(a)].
2. Tetrahedral holes are formed when a sphere sits in the dimple formed by three spheres in an adjacent layer [Fig. 10.35(b)].
3. Octahedral holes are formed between two sets of three spheres in adjoining layers of the closest packed structures [Fig. 10.35(c)].

For spheres of a given diameter, the holes increase in size in the order

$$\text{trigonal} < \text{tetrahedral} < \text{octahedral}$$

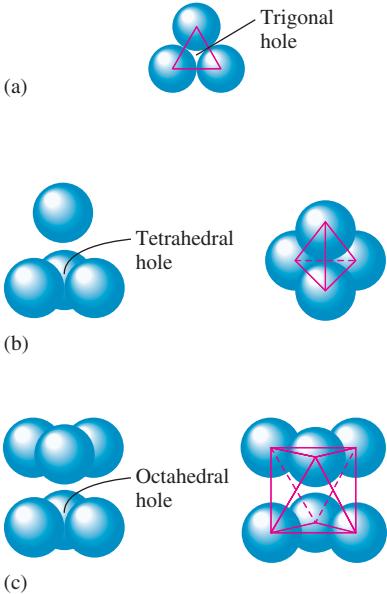
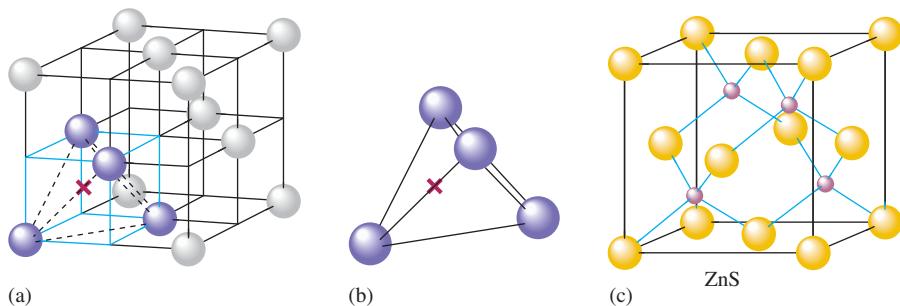


FIGURE 10.35

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 formed by three spheres in an adjacent layer. (c) The octahedral hole formed by six spheres in two adjacent layers.

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 = 180 pm) are arranged in a cubic closest packed structure with the smaller Zn^{2+} ions (ionic radius = 70 pm) in the tetrahedral holes. The locations of the tetrahedral holes in the face-centered cubic unit cell of the ccp structure are shown in Fig. 10.36(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

**FIGURE 10.36**

(a) The location (X) of a tetrahedral hole in the face-centered cubic unit cell. (b) One of the tetrahedral holes. (c) The unit cell for ZnS where the S²⁻ ions (yellow) are closest packed with the Zn²⁺ ions (red) in alternating tetrahedral holes.

Closest packed structures contain twice as many tetrahedral holes as packed spheres. Closest packed structures contain the same number of octahedral holes as packed spheres.

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 S²⁻ ions and Zn²⁺ ions to achieve electrical neutrality. Thus in the zinc sulfide structure only *half* the tetrahedral holes contain Zn²⁺ ions, as shown in Fig. 10.36(c).

The structure of sodium chloride can be described in terms of a cubic closest packed array of Cl⁻ ions with Na⁺ ions in all the octahedral holes. The locations of the octahedral holes in the face-centered cubic unit cell are shown in Fig. 10.37(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 10.37(b) shows the structure for sodium chloride that results from Na⁺ ions filling all the octahedral holes in a CCP array of Cl⁻ ions.

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 10.3

Determining the Number of Ions in a Unit Cell

Determine the net number of Na⁺ and Cl⁻ ions in the sodium chloride unit cell.

Solution

Note from Fig. 10.37(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

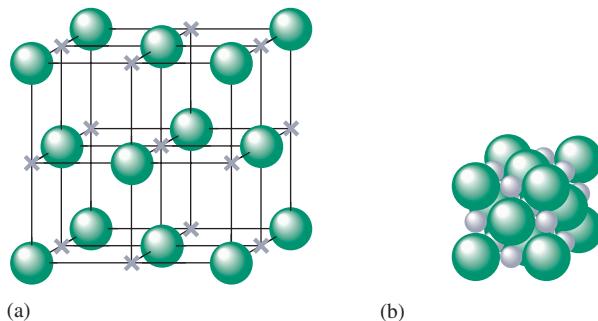
$$8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 4$$



Visualization: Structure of an Ionic Solid (NaCl).

FIGURE 10.37

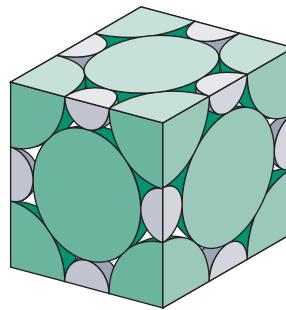
(a) The locations (gray X) of the octahedral holes in the face-centered cubic unit cell. (b) Representation of the unit cell for solid NaCl. The Cl⁻ ions (green spheres) have a CCP arrangement with Na⁺ ions (gray spheres) in all the octahedral holes. Note that this representation shows the idealized closest packed structure of NaCl. In the actual structure, the Cl⁻ ions do not quite touch.



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, whereas 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

$$1(1) + 12\left(\frac{1}{4}\right) = 4$$

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.



See Exercises 10.61 through 10.68.

In this chapter we have considered various types of solids. Table 10.7 summarizes these types of solids and some of their properties.

TABLE 10.7 Types and Properties of Solids

Type of Solid:	Atomic			Molecular	Ionic
Structural Unit:	Network	Metallic	Group 8A		
Type of Bonding:	Atom	Atom	Atom	Molecule	Ion
	Directional covalent bonds	Nondirectional covalent bonds involving electrons that are delocalized throughout the crystal	London dispersion forces	Polar molecules: dipole–dipole interactions Nonpolar molecules: London dispersion forces	Ionic
Typical Properties:	Hard High melting point	Wide range of hardness Wide range of melting points	Very low melting point	Soft Low melting point	Hard High melting point
Examples:	Insulator Diamond	Conductor Silver Iron Brass	Argon(s)	Ice (solid H_2O) Dry ice (solid CO_2)	Insulator Sodium chloride Calcium fluoride

Sample Exercise 10.4**Types of Solids**

Using Table 10.7, 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.

See Exercises 10.71 and 10.72.

10.8 Vapor Pressure and Changes of State

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, a process called **vaporization**, or **evaporation**. Vaporization 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 (40.7 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. 10.38). This evaporation process occurs at a constant rate at a given temperature (see Fig. 10.39). However, the reverse process is different. Initially, 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 re-form 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. 10.39). At this point no further net change occurs in the amount of liquid or vapor because the two 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.

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.

ΔH_{vap} for water at 100°C is 40.7 kJ/mol.

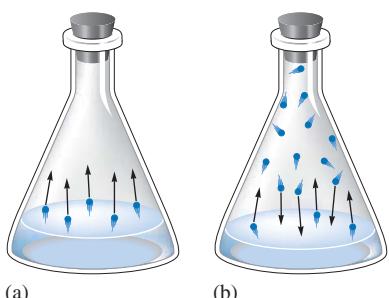
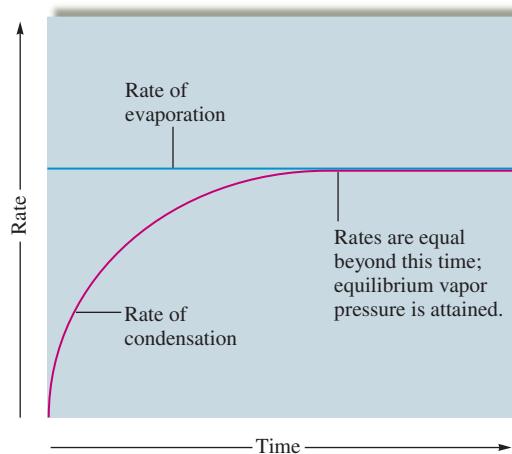


FIGURE 10.38

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.

**FIGURE 10.39**

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.

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 in Fig. 10.40(a). The liquid is injected at the bottom of the tube of mercury and floats to the surface because the mercury is so dense. A portion of 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

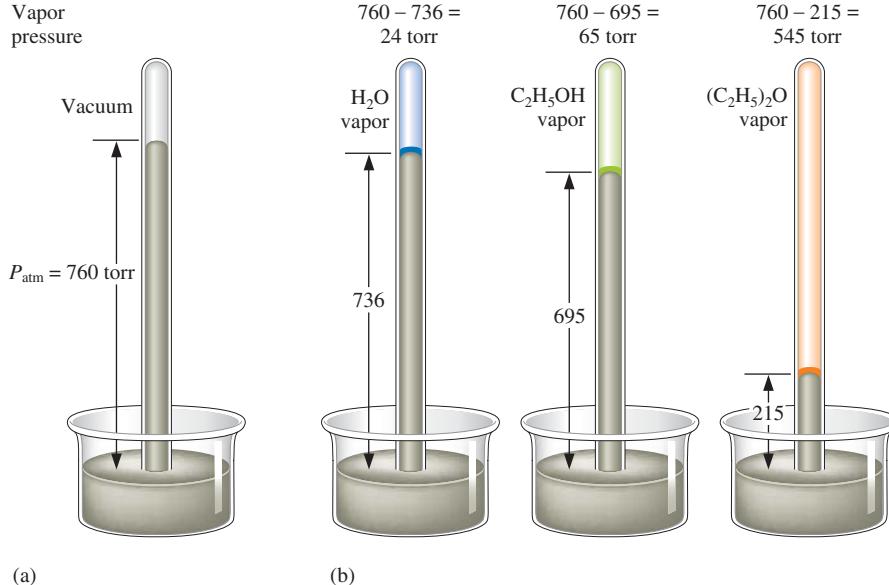
A system at equilibrium is dynamic on the molecular level but shows no macroscopic changes.

$$P_{\text{atmosphere}} = P_{\text{vapor}} + P_{\text{Hg column}}$$

Thus

$$P_{\text{vapor}} = P_{\text{atmosphere}} - P_{\text{Hg column}}$$

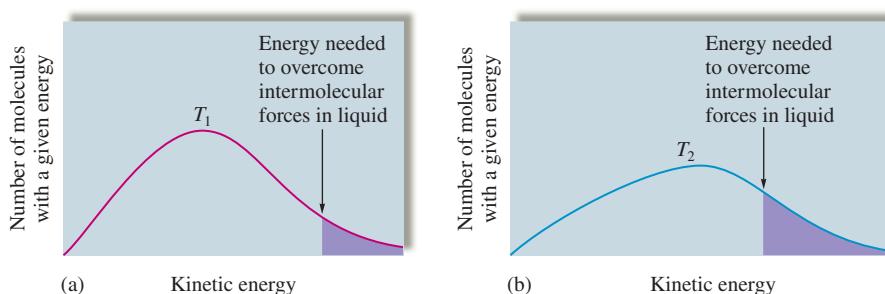
The vapor pressures of liquids vary widely [see Fig. 10.40(b)]. Liquids with high vapor pressures are said to be *volatile*—they evaporate rapidly from an open dish. The vapor pressure of a liquid is principally determined by the size of the *intermolecular forces* in the liquid. Liquids in which the intermolecular forces are large have relatively low vapor

**FIGURE 10.40**

(a) The vapor pressure of a liquid can be measured easily using a simple barometer of the type shown here. (b) The three liquids, water, ethanol ($\text{C}_2\text{H}_5\text{OH}$), and diethyl ether [$(\text{C}_2\text{H}_5)_2\text{O}$], have quite different vapor pressures. Ether is by far the most volatile of the three. Note that in each case a little liquid remains (floating on the mercury).

FIGURE 10.41

The number of molecules in a liquid with a given energy versus kinetic energy at two temperatures. Part (a) shows a lower temperature than that in part (b). Note that the proportion of molecules with enough energy to escape the liquid to the vapor phase (indicated by shaded areas) increases dramatically with temperature. This causes vapor pressure to increase markedly with temperature.



pressures because the molecules need high energies to escape to the vapor phase. For example, although water has a much lower molar mass than 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. 10.40(b)]. In general, substances with large molar masses have relatively low vapor pressures, mainly because of the large dispersion forces. The more electrons a substance has, the more polarizable it is, and the greater the dispersion forces are.

Measurements of the vapor pressure for a given liquid at several temperatures show that *vapor pressure increases significantly with temperature*. Figure 10.41 illustrates the distribution of molecular kinetic energy present in a liquid at two different temperatures. To overcome the intermolecular forces in a liquid, a molecule must have sufficient kinetic energy. As the temperature of the liquid is increased, the fraction of molecules having the minimum energy needed to overcome these forces and escape to the vapor phase increases markedly. Thus the vapor pressure of a liquid increases dramatically with temperature. Values for water at several temperatures are given in Table 10.8.

The quantitative nature of the temperature dependence of vapor pressure can be represented graphically. Plots of vapor pressure versus temperature for water, ethanol, and diethyl ether are shown in Fig. 10.42(a). Note the nonlinear increase in 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. 10.42(b). We can represent this behavior by the equation

$$\ln(P_{\text{vap}}) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} \right) + C \quad (10.4)$$

where ΔH_{vap} is the enthalpy 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 is taken.

Equation (10.4) is the equation for a straight line of the form $y = mx + b$, where

$$y = \ln(P_{\text{vap}})$$

$$x = \frac{1}{T}$$

$$m = \text{slope} = -\frac{\Delta H_{\text{vap}}}{R}$$

$$b = \text{intercept} = C$$

TABLE 10.8 The Vapor Pressure of Water as a Function of Temperature

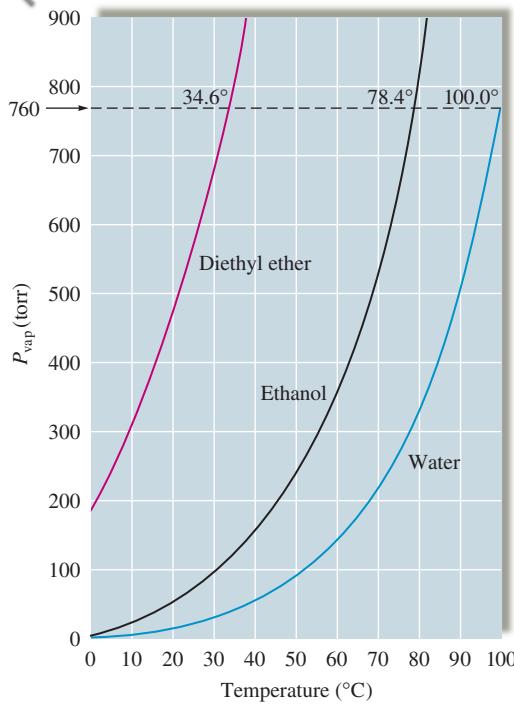
T (°C)	P (torr)
0.0	4.579
10.0	9.209
20.0	17.535
25.0	23.756
30.0	31.824
40.0	55.324
60.0	149.4
70.0	233.7
90.0	525.8

Natural logarithms are reviewed in Appendix 1.2.

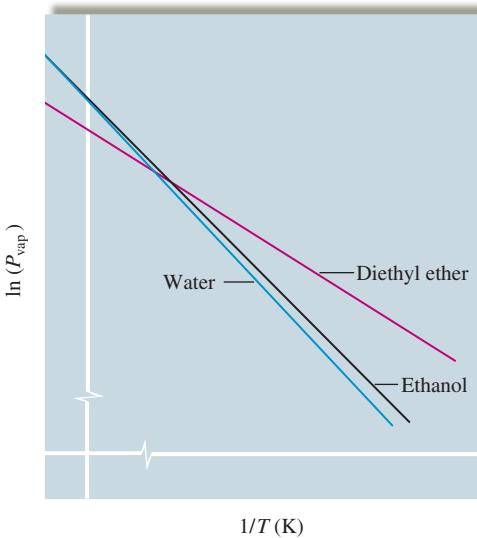
Sample Exercise 10.5

Determining Enthalpies of Vaporization

Using the plots in Fig. 10.42(b), determine whether water or diethyl ether has the larger enthalpy of vaporization.



(a)



(b)

FIGURE 10.42

(a) The vapor pressure of water, ethanol, and diethyl ether as a function of temperature. (b) Plots of $\ln(P_{\text{vap}})$ versus $1/T$ (Kelvin temperature) for water, ethanol, and diethyl ether.

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. 10.42(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 enthalpy of vaporization.

See Exercise 10.79.

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 values 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

$$\ln\left(\frac{P_{\text{vap},T_1}}{P_{\text{vap},T_2}}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (10.5)$$

Equation (10.5) is called the *Clausius–Clapeyron equation*.

Sample Exercise 10.6

Calculating Vapor Pressure

The vapor pressure of water at 25°C is 23.8 torr, and the heat of vaporization of water at 25°C is 43.9 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

$$\begin{aligned} P_{\text{vap},T_1} &= 23.8 \text{ torr} \\ T_1 &= 25 + 273 = 298 \text{ K} \\ T_2 &= 50. + 273 = 323 \text{ K} \\ \Delta H_{\text{vap}} &= 43.9 \text{ kJ/mol} = 43,900 \text{ J/mol} \\ R &= 8.3145 \text{ J/K mol} \end{aligned}$$

Thus

$$\ln\left(\frac{23.8 \text{ torr}}{P_{\text{vap},T_2} (\text{torr})}\right) = \frac{43,900 \text{ J/mol}}{8.3145 \text{ J/K mol}} \left(\frac{1}{323 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

$$\ln\left(\frac{23.8}{P_{\text{vap},T_2}}\right) = -1.37$$

Taking the antilog (see Appendix 1.2) of both sides gives

$$\begin{aligned} \frac{23.8}{P_{\text{vap},T_2}} &= 0.254 \\ P_{\text{vap},T_2} &= 93.7 \text{ torr} \end{aligned}$$

See Exercises 10.81 through 10.84.

Phase changes of carbon dioxide are discussed in Section 10.9.

Sublimation: A process in which a substance goes directly from the solid to the gaseous state.

Like liquids, solids have vapor pressures. Figure 10.43 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).

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.

The heating curve for water is given in Fig. 10.44. As energy flows into the ice, the random vibrations of the water molecules increase as 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



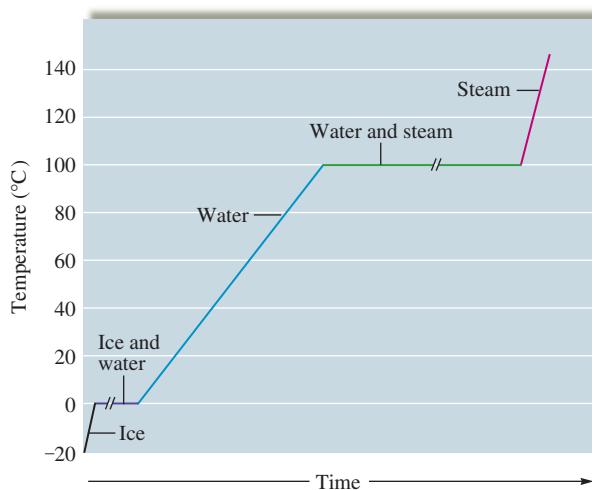
Visualization: Changes of State

**FIGURE 10.43**

Iodine being heated, causing it to sublime, forming crystals of $\text{I}_2(s)$ on the bottom of an evaporating dish cooled by ice.

Ionic solids such as NaCl and NaF have very high melting points and enthalpies of fusion because of the strong ionic forces in these solids. At the other extreme is $\text{O}_2(s)$, a molecular solid containing nonpolar molecules with weak intermolecular forces. (See Table 10.9.)

The melting and boiling points will be defined more precisely later in this section.

**FIGURE 10.44**

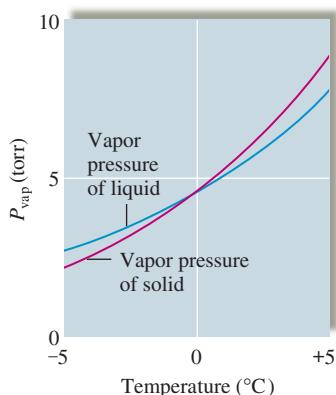
The heating curve (not drawn to scale) for a given quantity of water where energy is added at a constant rate. The plateau at the boiling point is longer than the plateau at the melting point because it takes almost seven times more energy (and thus seven times the heating time) to vaporize liquid water than to melt ice. The slopes of the other lines are different because the different states of water have different molar heat capacities (the energy required to raise the temperature of 1 mole of a substance by 1°C).

heating curve. At this temperature, called the *melting point*, all 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 at the melting point when a solid melts is called the **heat of fusion**, or more accurately, the **enthalpy of fusion**, ΔH_{fus} . The melting points and enthalpies of fusion for several representative solids are listed in Table 10.9.

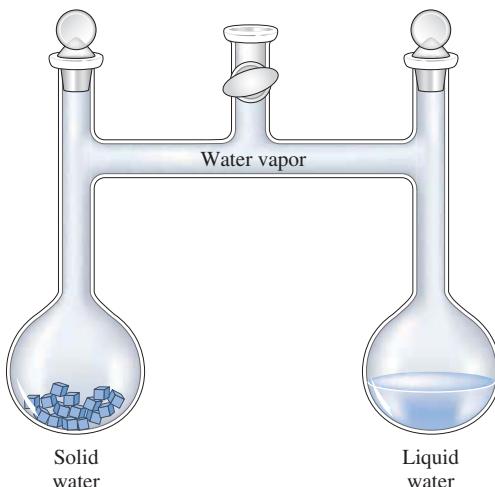
The temperature remains constant until the solid has completely changed to liquid; then it begins to increase again. At 100°C the liquid water reaches its *boiling point*, and the temperature then remains constant as the added energy is used to vaporize the liquid. When the liquid is completely changed to vapor, the temperature again begins to rise. Note that changes of state are physical changes; although 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

TABLE 10.9 Melting Points and Enthalpies of Fusion for Several Representative Solids

Compound	Melting Point (°C)	Enthalpy of Fusion (kJ/mol)
O_2	-218	0.45
HCl	-114	1.99
HI	-51	2.87
CCl_4	-23	2.51
CHCl_3	-64	9.20
H_2O	0	6.02
NaF	992	29.3
NaCl	801	30.2

**FIGURE 10.45**

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.

**FIGURE 10.46**

An apparatus that allows solid and liquid water to interact only through the vapor state.

be a chemical change, since covalent bonds are broken. We no longer have water after this occurs.

The melting and boiling points for a substance are determined by the vapor pressures of the solid and liquid states. Figure 10.45 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.

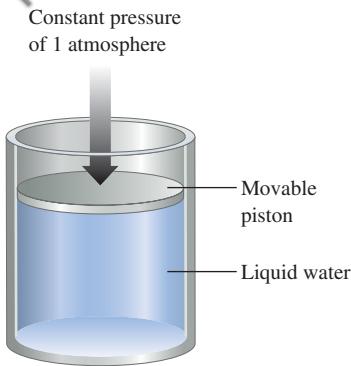
These concepts can be demonstrated experimentally using the apparatus illustrated in Fig. 10.46, where ice occupies one compartment and liquid water the other. Consider the following cases.

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.

**FIGURE 10.47**

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.



Boiling chip releasing air bubbles acts as a nucleating agent for the bubbles that form when water boils.

Case 3

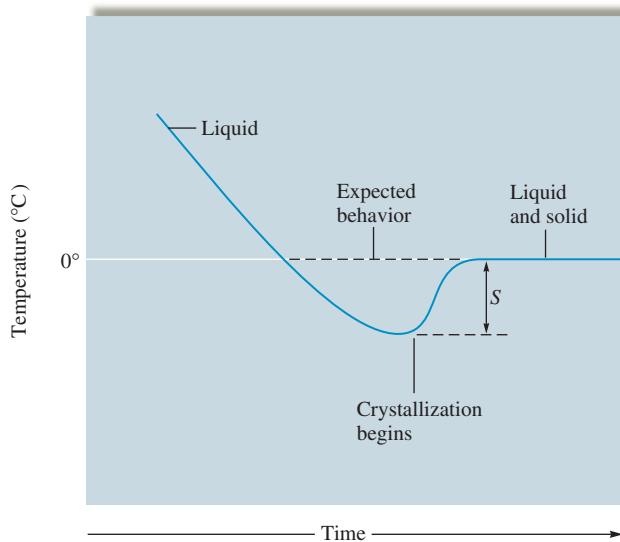
A temperature at which the vapor pressures of the solid and liquid are identical. In this case, the solid and liquid states have the same vapor pressure, so they can coexist in the apparatus at equilibrium simultaneously with the vapor. This temperature represents the freezing point where both the solid 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. 10.47. 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.

However, 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. 10.48).

A liquid also can 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.

**FIGURE 10.48**

The supercooling of water. The extent of supercooling is given by S .

10.9 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. 10.49) 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. 10.47, where no material can escape into the surroundings and no air is present. Notice that the diagram is not drawn to scale (neither axis is linear). This is done to emphasize certain features of the diagram that will be discussed below.

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. 10.50.

Experiment 1

Pressure is 1 atm. This experiment begins with the cylinder shown in Fig. 10.47 completely filled with ice at a temperature of -20°C and 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. Note that under these conditions no vapor exists in the system. The vapor pressures of the solid and liquid are equal, but this vapor pressure is less than 1 atm, so no water vapor can exist. This is true on the solid/liquid line everywhere except at the triple point (see Experiment 3 below). 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 atm, 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 known as *sublimation*. Sublimation occurs when the vapor pressure of ice is equal to the

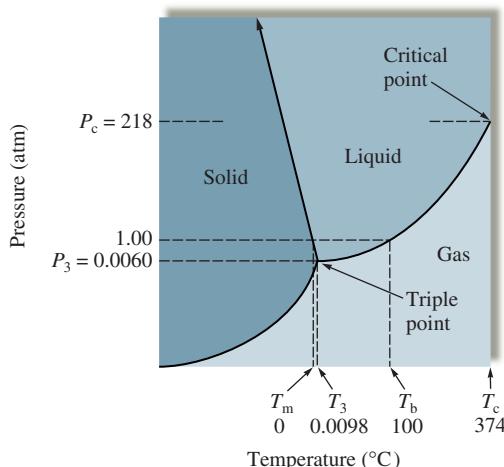
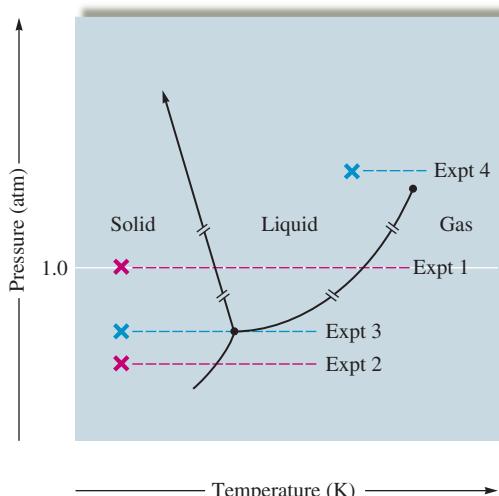


FIGURE 10.49

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. (Note that this line extends indefinitely, as indicated by the arrow.)

**FIGURE 10.50**

Diagrams of various heating experiments on samples of water in a closed system.

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 at temperatures above -10°C or freeze at temperatures below -10°C .

Experiment 3

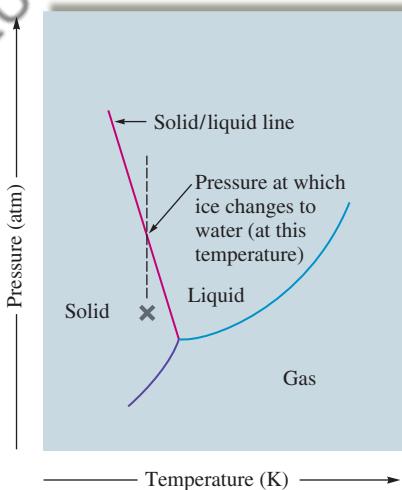
Pressure is 4.58 torr. Again, we start with ice as the only component in the cylinder at -20°C . In this case the pressure exerted on the ice by the piston is 4.58 torr. As the cylinder is heated, no new phase appears until the temperature reaches 0.01°C (273.16 K). At this point, called the **triple point**, solid and liquid water have identical vapor pressures of 4.58 torr. Thus *at 0.01°C (273.16 K) and 4.58 torr all three states of water are present*. In fact, *only under these conditions can all three states of water coexist in a closed system*.

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 ice *decreases* as the external pressure *increases*. This behavior, which is opposite to that

**FIGURE 10.51**

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.



Visualization: Boiling Water with Ice Water

Water boils at 89°C in Leadville, Colorado.



The effect of pressure on ice allows this skater to glide smoothly.

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 10.51 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 phenomenon may be important 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. Also, the frictional heating due to the moving skate contributes to the melting of the ice.* After the blade passes, the liquid refreezes as normal pressure and temperature return. Without this lubrication effect due to the thawing ice, ice skating would not be the smooth, graceful activity that many people enjoy.

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 10.10), 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 San Diego, California (sea level), since water boils at a lower temperature in Leadville.

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 and 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, although it is not the sublimation under equilibrium conditions described by the phase diagram.

*The physics of ice skating is quite complex, and there is disagreement about whether the pressure or the frictional heating of the ice skate is most important. See "Letter to the Editor," by R. Silberman, *J. Chem. Ed.* **65** (1988): 186.

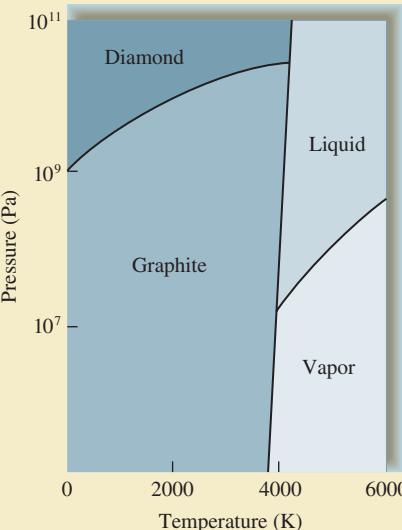


CHEMICAL IMPACT

Making Diamonds at Low Pressures: Fooling Mother Nature

In 1955 Robert H. Wentorf, Jr., accomplished something that borders on alchemy—he turned peanut butter into diamonds. He and his coworkers at the General Electric Research and Development Center also changed roofing pitch, wood, coal, and many other carbon-containing materials into diamonds, using a process involving temperatures of $\approx 2000^\circ\text{C}$ and pressures of $\approx 10^5$ atm. Although the first diamonds made by this process looked like black sand because of the impurities present, the process has now been developed to a point such that beautiful, clear, gem-quality diamonds can be produced. General Electric now has the capacity to produce 150 million carats (30,000 kg) of diamonds annually (virtually all of which is “diamond grit” used for industrial purposes such as abrasive coatings on cutting tools). The production of large, gem-quality diamonds by this process is still too expensive to compete with the natural sources of these stones. However, this may change as methods are developed for making diamonds at low pressures.

The high temperatures and pressures used in the GE process for making diamonds make sense if one looks at the accompanying phase diagram for carbon. Note that graphite—not diamond—is the most stable form of carbon



The phase diagram for carbon.

under ordinary conditions of temperature and pressure. However, diamond becomes more stable than graphite at very high pressures (as one would expect from the greater

TABLE 10.10 Boiling Point of Water at Various Locations

Location	Feet Above Sea Level	P_{atm} (torr)	Boiling Point ($^\circ\text{C}$)
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



A carbon dioxide fire extinguisher.

The Phase Diagram for Carbon Dioxide

The phase diagram for carbon dioxide (Fig. 10.52) 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

density of diamond). The high temperature used in the GE process is necessary to disrupt the bonds in graphite so that diamond (the most stable form of carbon at the high pressures used in the process) can form. Once the diamond is produced, the elemental carbon is “trapped” in this form at normal conditions (25°C , 1 atm) because the reaction back to the graphite form is so slow. That is, even though graphite is more stable than diamond at 25°C and 1 atm, diamond can exist almost indefinitely because the conversion to graphite is a very *slow* reaction. As a result, diamonds formed at the high pressures found deep in the earth’s crust can be brought to the earth’s surface by natural geologic processes and continue to exist for millions of years.*

We have seen that diamond formed in the laboratory at high pressures is “trapped” in this form, but this process is very expensive. Can diamond be formed at low pressures? The phase diagram for carbon says no. However, researchers have found that under the right conditions diamonds can be

*In Morocco, a 50-km-long slab called Beni Bousera contains chunks of graphite that were probably once diamonds formed in the deposit when it was buried 150 km underground. As this slab slowly rose to the surface over millions of years, the very slow reaction changing diamond to graphite had time to occur. On the other hand, in the diamond-rich kimberlite deposits in South Africa, which rise to the surface much faster, the diamonds have not had sufficient time to revert to graphite.

“grown” at low pressures. The process used is called *chemical vapor deposition (CVD)*. CVD uses an energy source to release carbon atoms from a compound such as methane into a steady flow of hydrogen gas (some of which is dissociated to produce hydrogen atoms). The carbon atoms then deposit as a diamond film on a surface maintained at a temperature between 600 and 900°C . Why does diamond form on this surface rather than the favored graphite? Nobody is sure, but it has been suggested that at these relatively high temperatures the diamond structure grows faster than the graphite structure and so diamond is favored under these conditions. It also has been suggested that the hydrogen atoms present react much faster with graphite fragments than with diamond fragments, effectively removing any graphite from the growing film. Once it forms, of course, diamond is trapped. The major advantage of CVD is that there is no need for the extraordinarily high pressures used in the traditional process for synthesizing diamonds.

The first products with diamond films are already on the market. Audiophiles can buy tweeters that have diaphragms coated with a thin diamond film that limits sound distortion. Watches with diamond-coated crystals are planned, as are diamond-coated windows in infrared scanning devices used in analytical instruments and missile guidance systems. These applications represent only the beginning for diamond-coated products.

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.

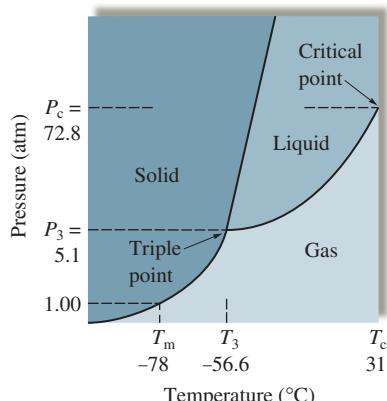


FIGURE 10.52

The phase diagram for carbon dioxide. The liquid state does not exist at a pressure of 1 atm. The solid/liquid line has a positive slope, since the density of solid carbon dioxide is greater than that of liquid carbon dioxide.

Key Terms

Section 10.1

condensed states
intermolecular forces
dipole–dipole attraction
hydrogen bonding
London dispersion forces

Section 10.2

surface tension
capillary action
viscosity

Section 10.3

crystalline solid
amorphous solid
lattice
unit cell
X-ray diffraction
ionic solid
molecular solid
atomic solid

Section 10.4

closest packing
hexagonal closest packed (hcp) structure
cubic closest packed (ccp) structure
band model
molecular orbital (MO) model
alloy
substitutional alloy
interstitial alloy

Section 10.5

network solid
silica
silicate
glass
ceramic
semiconductor
n-type semiconductor
p-type semiconductor
p–n junction

Section 10.8

vaporization (evaporation)
heat of vaporization
enthalpy of vaporization (ΔH_{vap})
condensation
equilibrium
equilibrium vapor pressure
sublimation
heating curve
enthalpy (heat) of fusion (ΔH_{fus})
normal melting point
normal boiling point
supercooled
superheated

For Review

Condensed states of matter: liquids and solids

- Held together by forces among the component molecules, atoms, or ions
- Liquids exhibit properties such as surface tension, capillary action, and viscosity that depend on the forces among the components

Dipole–dipole forces

- Attractions among molecules with dipole moments
- Hydrogen bonding is a particularly strong form of dipole–dipole attraction
 - Occurs in molecules containing hydrogen bonded to a highly electronegative element such as nitrogen, oxygen, or fluorine
 - Produces unusually high boiling points

London dispersion forces

- Caused by instantaneous dipoles that form in atoms or nonpolar molecules

Crystalline solids

- Have a regular arrangement of components often represented as a lattice; the smallest repeating unit of the lattice is called the unit cell
- Classified by the types of components:
 - Atomic solids (atoms)
 - Ionic solids (ions)
 - Molecular solids (molecules)
- Arrangement of the components can be determined by X-ray analysis

Metals

- Structure is modeled by assuming atoms to be uniform spheres
 - Closest packing
 - Hexagonal
 - Cubic
- Metallic bonding can be described in terms of two models
 - Electron sea model: valence electrons circulate freely among the metal cations
 - Band model: electrons are assumed to occupy molecular orbitals
 - Conduction bands: closely spaced molecular orbitals with empty electron spaces
- Alloys: mixtures with metallic properties
 - Substitutional
 - Interstitial

Network solids

- Contain giant networks of atoms covalently bound together
- Examples are diamond and graphite
- Silicates are network solids containing Si—O—Si bridges that form the basis for many rocks, clays, and ceramics

Semiconductors

- Very pure silicon is “doped” with other elements
 - n-type: doping atoms typically contain five valence electrons (one more than silicon)
 - p-type: doping elements typically contain three valence electrons
- Modern electronics are based on devices with p–n junctions

Molecular solids

- Components are discrete molecules
- Intermolecular forces are typically weak, leading to relatively low boiling and melting points

Section 10.9

phase diagram
triple point
critical temperature
critical pressure
critical point

Ionic solids

- Components are ions
- Interionic forces are relatively strong, leading to solids with high melting and boiling points
- Many structures consist of closest packing of the larger ions with the smaller ions in tetrahedral or octahedral holes

Phase changes

- The change from liquid to gas (vapor) is called vaporization or evaporation
- Condensation is the reverse of vaporization
- Equilibrium vapor pressure: the pressure that occurs over a liquid or solid in a closed system when the rate of evaporation equals the rate of condensation
 - Liquids whose components have high intermolecular forces have relatively low vapor pressures
 - Normal boiling point: the temperature at which the vapor pressure of a liquid equals one atmosphere
 - Normal melting point: the temperature at which a solid and its liquid have the same vapor pressure (at 1 atm external pressure)
- Phase diagram
 - Shows what state exists at a given temperature and pressure in a closed system
 - Triple point: temperature at which all three phases exist simultaneously
 - Critical point: defined by the critical temperature and pressure
 - Critical temperature: the temperature above which the vapor cannot be liquefied no matter the applied pressure
 - Critical pressure: the pressure required to produce liquefaction at the critical temperature

REVIEW QUESTIONS

1. What are intermolecular forces? How do they differ from intramolecular forces? What are dipole–dipole forces? How do typical dipole–dipole forces differ from hydrogen-bonding interactions? In what ways are they similar? What are London dispersion forces? How do typical London dispersion forces differ from dipole–dipole forces? In what ways are they similar? Describe the relationship between molecular size and strength of London dispersion forces. Place 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 an example of such an instance.
2. Define the following terms and describe how each depends on the strength of the intermolecular forces.
 - a. surface tension
 - b. viscosity
 - c. melting point
 - d. boiling point
 - e. vapor pressure
3. Compare and contrast solids versus liquids versus gases.
4. Distinguish between the items in the following pairs.
 - a. crystalline solid; amorphous solid
 - b. ionic solid; molecular solid
 - c. molecular solid; network solid
 - d. metallic solid; network solid
5. What is a lattice? What is a unit cell? Describe a simple cubic unit cell. How many net atoms are contained in a simple cubic unit cell? How is the radius of the atom

related to the cube edge length for a simple cubic unit cell? Answer the same questions for the body-centered cubic unit cell and for the face-centered unit cell.

6. What is closest packing? What is the difference between hexagonal closest packing and cubic closest packing? What is the unit cell for each closest packing?
7. Use the band model to describe differences among insulators, conductors, and semiconductors. Also 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

How do conductors and semiconductors differ as to the effect of temperature on electrical conductivity? How can an n-type semiconductor be produced from pure germanium? How can a p-type semiconductor be produced from pure germanium?
8. Describe, in general, the structures of ionic solids. Compare and contrast the structure of sodium chloride and zinc sulfide. How many tetrahedral holes and octahedral holes are there per closest packed anion? In zinc sulfide, why are only one-half of the tetrahedral holes filled with cations?
9. Define each of the following.
 - a. evaporation
 - b. condensation
 - c. sublimation
 - d. boiling
 - e. melting
 - f. enthalpy of vaporization
 - g. enthalpy of fusion
 - h. heating curve

Why is the enthalpy of vaporization for water much greater than its enthalpy of fusion? What does this say about the changes in intermolecular forces in going from solid to liquid to vapor? What do we mean when we say that a liquid is *volatile*? Do volatile liquids have large or small vapor pressures at room temperature? What strengths of intermolecular forces occur in highly volatile liquids?

10. Compare and contrast the phase diagrams of water versus carbon dioxide. Why doesn't CO_2 have a normal melting point and a normal boiling point, whereas water does? The slopes of the solid–liquid lines in the phase diagrams of H_2O and CO_2 are different. What do the slopes of the solid–liquid lines indicate in terms of the relative densities of the solid and liquid states for each substance? How do the melting points of H_2O and CO_2 depend on pressure? How do the boiling points of H_2O and CO_2 depend on pressure? Rationalize why the critical temperature for H_2O is greater than that for CO_2 .

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. It is possible to balance a paper clip on the surface of water in a beaker. If you add a bit of soap to the water, however, the paper clip sinks. Explain how the paper clip can float and why it sinks when soap is added.

2. Consider a sealed container half-filled with water. Which statement best describes what occurs in the container?
 - a. Water evaporates until the air is saturated with water vapor; at this point, no more water evaporates.
 - b. Water evaporates until the air is overly saturated (supersaturated) with water, and most of this water recondenses; this cycle continues until a certain amount of water vapor is present, and then the cycle ceases.
 - c. Water does not evaporate because the container is sealed.
 - d. Water evaporates, and then water evaporates and recondenses simultaneously and continuously.

- e. Water evaporates until it is eventually all in vapor form. Explain each choice. Justify your choice, and for choices you did not pick, explain what is wrong with them.
3. Explain the following: You add 100 mL of water to a 500-mL round-bottom flask and heat the water until it is boiling. You remove the heat and stopper the flask, and the boiling stops. You then run cool water over the neck of the flask, and the boiling begins again. It seems as though you are boiling water by cooling it.
4. Is it possible for the dispersion forces in a particular substance to be stronger than the hydrogen bonding forces in another substance? Explain your answer.
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. Why do liquids have a vapor pressure? Do all liquids have vapor pressures? Explain. Do solids exhibit vapor pressure? Explain. How does vapor pressure change with changing temperature? Explain.
7. Water in an open beaker evaporates over time. As the water is evaporating, is the vapor pressure increasing, decreasing, or staying the same? Why?
8. What is the vapor pressure of water at 100°C? How do you know?
9. Refer to Fig. 10.44. Why doesn't temperature increase continuously over time? That is, why does the temperature stay constant for periods of time?
10. Which are stronger, intermolecular or intramolecular forces for a given molecule? What observation(s) have you made that support this? Explain.
11. Why does water evaporate?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

12. The nonpolar hydrocarbon $C_{25}H_{52}$ is a solid at room temperature. Its boiling point is greater than 400°C. Which has the stronger intermolecular forces, $C_{25}H_{52}$ or H_2O ? Explain your answer.
13. Atoms are assumed to touch in closest packed structures, yet every closest packed unit cell contains a significant amount of empty space. Why?
14. 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?
15. Use the kinetic molecular theory to explain why a liquid gets cooler as it evaporates from an insulated container.
16. Will a crystalline solid or an amorphous solid give a simpler X-ray diffraction pattern? Why?
17. What is an alloy? Explain the differences in structure between substitutional and interstitial alloys. Give an example of each type.
18. Describe what is meant by a dynamic equilibrium in terms of the vapor pressure of a liquid.

19. How does each of the following affect the rate of evaporation of a liquid in an open dish?
- intermolecular forces
 - temperature
 - surface area
20. When a person has a severe fever, one therapy used to reduce the fever is an "alcohol rub." Explain how the evaporation of alcohol from a person's skin removes heat energy from the body.
21. When wet laundry is hung on a clothesline on a cold winter day, it will freeze but eventually dry. Explain.
22. Why is a burn from steam typically much more severe than a burn from boiling water?
23. You have three covalent compounds with three very different boiling points. All of the compounds have similar molar mass and relative shape. Explain how these three compounds could have very different boiling points.
24. Compare and contrast the structures of the following solids.
- diamond versus graphite
 - silica versus silicates versus glass
25. Compare and contrast the structures of the following solids.
- $CO_2(s)$ versus $H_2O(s)$
 - $NaCl(s)$ versus $CsCl(s)$; See Exercise 61 for the structures.
26. Silicon carbide (SiC) is an extremely hard substance that acts as an electrical insulator. Propose a structure for SiC .
27. A plot of $\ln P_{vap}$ versus $1/T$ (K) is linear with a negative slope. Why is this the case?
28. Iodine, like most substances, exhibits only three phases; solid, liquid, and vapor. The triple point of iodine is at 90 torr and 115°C. Which of the following statements concerning liquid I_2 must be true? Explain your answer.
- $I_2(l)$ is more dense than $I_2(g)$.
 - $I_2(l)$ cannot exist above 115°C.
 - $I_2(l)$ cannot exist at 1 atmosphere pressure.
 - $I_2(l)$ cannot have a vapor pressure greater than 90 torr.
 - $I_2(l)$ cannot exist at a pressure of 10 torr.

Exercises

In this section similar exercises are paired.

Intermolecular Forces and Physical Properties

29. Identify the most important types of interparticle forces present in the solids of each of the following substances.
- | | |
|-------------|-------------|
| a. Ar | e. CH_4 |
| b. HCl | f. CO |
| c. HF | g. $NaNO_3$ |
| d. $CaCl_2$ | |
30. Identify the most important types of interparticle forces present in the solids of each of the following substances.
- | |
|---|
| a. NH_4Cl |
| b. Teflon, $CF_3(CF_2CF_2)_nCF_3$ |
| c. Polyethylene, $CH_3(CH_2CH_2)_nCH_3$ |
| d. $CHCl_3$ |
| e. NH_3 |
| f. NO |
| g. BF_3 |

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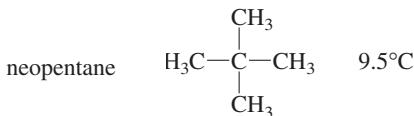
- 31.** Predict which substance in each of the following pairs would have the greater intermolecular forces.

- CO_2 or OCS
- SeO_2 or SO_2
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ or $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$
- CH_3CH_3 or H_2CO
- CH_3OH or H_2CO

- 32.** Consider the compounds Cl_2 , HCl , F_2 , NaF , and HF . Which compound has a boiling point closest to that of argon? Explain.

- 33.** Rationalize the difference in boiling points for each of the following pairs of substances:

- a. *n*-pentane $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ 36.2°C



- b. HF 20°C
 HCl -85°C
 c. HCl -85°C
 LiCl 1360°C
 d. *n*-pentane $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ 36.2°C
n-hexane $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ 69°C

- 34.** Consider the following compounds and formulas. (*Note:* The formulas are written in such a way as to give you an idea of the structure.)

- ethanol: $\text{CH}_3\text{CH}_2\text{OH}$
 dimethyl ether: CH_3OCH_3
 propane: $\text{CH}_3\text{CH}_2\text{CH}_3$

The boiling points of these compounds are (in no particular order) -42.1°C , -23°C , and 78.5°C . Match the boiling points to the correct compounds.

- 35.** In each of the following groups of substances, pick the one that has the given property. Justify your answer.

- highest boiling point: HBr , Kr , or Cl_2
- highest freezing point: H_2O , NaCl , or HF
- lowest vapor pressure at 25°C : Cl_2 , Br_2 , or I_2
- lowest freezing point: N_2 , CO , or CO_2
- lowest boiling point: CH_4 , CH_3CH_3 , or $\text{CH}_3\text{CH}_2\text{CH}_3$
- highest boiling point: HF , HCl , or HBr

- g. lowest vapor pressure at 25°C : $\text{CH}_3\text{CH}_2\text{CH}_3$, CH_3CCH_3 , or $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

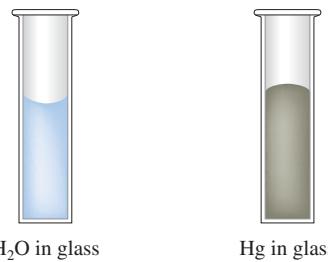
- 36.** In each of the following groups of substances, pick the one that has the given property. Justify each answer.

- highest boiling point: CCl_4 , CF_4 , CBr_4
- lowest freezing point: LiF , F_2 , HCl
- smallest vapor pressure at 25°C : CH_3OCH_3 , $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{CH}_3$
- greatest viscosity: H_2S , HF , H_2O_2

- greatest heat of vaporization: H_2CO , CH_3CH_3 , CH_4
- smallest enthalpy of fusion: I_2 , CsBr , CaO

Properties of Liquids

- 37.** The shape of the meniscus of water in a glass tube is different from that of mercury in a glass tube. Why?



- 38.** Explain why water forms into beads on a waxed car finish.

- 39.** 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.

- 40.** Carbon diselenide (CSe_2) is a liquid at room temperature. The normal boiling point is 125°C , and the melting point is -45.5°C . Carbon disulfide (CS_2) is also a liquid at room temperature with normal boiling and melting points of 46.5°C and -111.6°C , respectively. How do the strengths of the intermolecular forces vary from CO_2 to CS_2 to CSe_2 ? Explain.

Structures and Properties of Solids

- 41.** X rays from a copper X-ray tube ($\lambda = 154 \text{ pm}$) 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?

- 42.** The second-order diffraction ($n = 2$) for a gold crystal is at an angle of 22.20° for X rays of 154 pm . What is the spacing between these crystal planes?

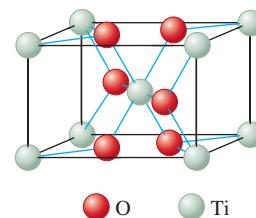
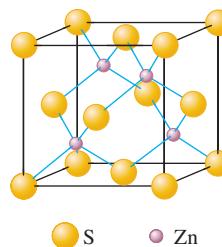
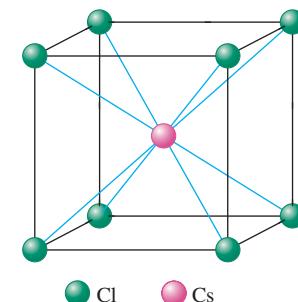
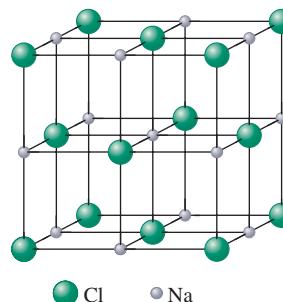
- 43.** A topaz crystal has an interplanar spacing (d) of 1.36 \AA ($1 \text{ \AA} = 1 \times 10^{-10} \text{ m}$). Calculate the wavelength of the X ray that should be used if $\theta = 15.0^\circ$ (assume $n = 1$).

- 44.** X rays of wavelength 2.63 \AA were used to analyze a crystal. The angle of first-order diffraction ($n = 1$ in the Bragg equation) was 15.55° degrees. What is the spacing between crystal planes, and what would be the angle for second-order diffraction ($n = 2$)?

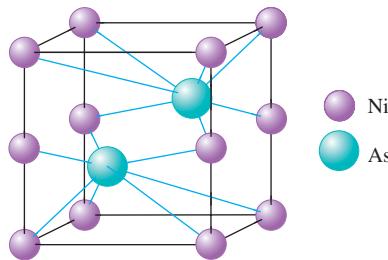
- 45.** Calcium has a cubic closest packed structure as a solid. Assuming that calcium has an atomic radius of 197 pm , calculate the density of solid calcium.

- 46.** 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.

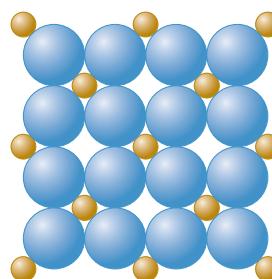
- 47.** A certain form of lead has a cubic closest packed structure with an edge length of 492 pm. Calculate the value of the atomic radius and the density of lead.
- 48.** You are given a small bar of an unknown metal X. You find the density of the metal to be 10.5 g/cm³. An X-ray diffraction experiment measures the edge of the face-centered cubic unit cell as 4.09 Å (1 Å = 10⁻¹⁰ m). Identify X.
- 49.** Titanium metal has a body-centered cubic unit cell. The density of titanium is 4.50 g/cm³. 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.)
- 50.** Barium has a body-centered cubic structure. If the atomic radius of barium is 222 pm, calculate the density of solid barium.
- 51.** The radius of gold is 144 pm, and the density is 19.32 g/cm³. Does elemental gold have a face-centered cubic structure or a body-centered cubic structure?
- 52.** The radius of tungsten is 137 pm and the density is 19.3 g/cm³. Does elemental tungsten have a face-centered cubic structure or a body-centered cubic structure?
- 53.** What fraction of the total volume of a cubic closest packed structure is occupied by atoms? (*Hint:* $V_{\text{sphere}} = \frac{4}{3}\pi r^3$.) What fraction of the total volume of a simple cubic structure is occupied by atoms? Compare the answers.
- 54.** Iron has a density of 7.86 g/cm³ and crystallizes in a body-centered cubic lattice. Show that only 68% of a body-centered lattice is actually occupied by atoms, and determine the atomic radius of iron.
- 55.** Explain how doping silicon with either phosphorus or gallium increases the electrical conductivity over that of pure silicon.
- 56.** Explain how a p–n junction makes an excellent rectifier.
- 57.** Selenium is a semiconductor used in photocopying machines. What type of semiconductor would be formed if a small amount of indium impurity is added to pure selenium?
- 58.** The Group 3A/Group 5A semiconductors are composed of equal amounts of atoms from Group 3A and Group 5A—for example, InP and GaAs. These types of semiconductors are used in light-emitting diodes and solid-state lasers. What would you add to make a p-type semiconductor from pure GaAs? How would you dope pure GaAs to make an n-type semiconductor?
- 59.** The band gap in aluminum phosphide (AlP) is 2.5 electron-volts (1 eV = 1.6 × 10⁻¹⁹ J). What wavelength of light is emitted by an AlP diode?
- 60.** An aluminum antimonide solid-state laser emits light with a wavelength of 730. nm. Calculate the band gap in joules.
- 61.** 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.



- 62.** The unit cell for nickel arsenide is shown below. What is the formula of this compound?



- 63.** Cobalt fluoride crystallizes in a closest packed array of fluoride ions with the cobalt ions filling one-half of the octahedral holes. What is the formula of this compound?
- 64.** The compounds Na₂O, CdS, and ZrI₄ all can be described as cubic closest packed anions with the cations in tetrahedral holes. What fraction of the tetrahedral holes is occupied for each case?
- 65.** What is the formula for the compound that crystallizes with a cubic closest packed array of sulfur ions, and that contains zinc ions in $\frac{1}{8}$ of the tetrahedral holes and aluminum ions in $\frac{1}{2}$ of the octahedral holes?
- 66.** Assume the two-dimensional structure of an ionic compound, M_xA_y, is



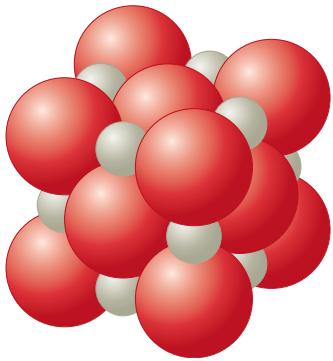
What is the empirical formula of this ionic compound?

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67. A certain metal fluoride crystallizes in such a way that the fluoride ions occupy simple cubic lattice sites, while the metal ions occupy the body centers of *half* the cubes. What is the formula of the metal fluoride?

68. The structure of manganese fluoride can be described as a simple cubic array of manganese ions with fluoride ions at the center of each edge of the cubic unit cell. What is the charge of the manganese ions in this compound?

69. The unit cell of MgO is shown below.



Does MgO have a structure like that of NaCl or ZnS? If the density of MgO is 3.58 g/cm³, estimate the radius (in centimeters) of the O²⁻ anions and the Mg²⁺ cations.

70. The CsCl structure is a simple cubic array of chloride ions with a cesium ion at the center of each cubic array (see Exercise 61). Given that the density of cesium chloride is 3.97 g/cm³, and assuming that the chloride and cesium ions touch along the body diagonal of the cubic unit cell, calculate the distance between the centers of adjacent Cs⁺ and Cl⁻ ions in the solid. Compare this value with the expected distance based on the sizes of the ions. The ionic radius of Cs⁺ is 169 pm, and the ionic radius of Cl⁻ is 181 pm.

71. What type of solid will each of the following substances form?

- a. CO₂
- e. Ru
- i. NaOH
- b. SiO₂
- f. I₂
- j. U
- c. Si
- g. KBr
- k. CaCO₃
- d. CH₄
- h. H₂O
- l. PH₃

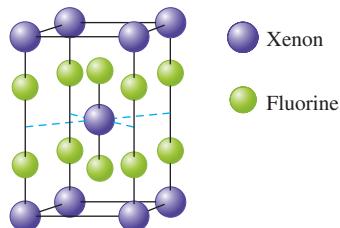
72. What type of solid will each of the following substances form?

- a. diamond
- e. KCl
- i. Ar
- b. PH₃
- f. quartz
- j. Cu
- c. H₂
- g. NH₄NO₃
- k. C₆H₁₂O₆
- d. Mg
- h. SF₂

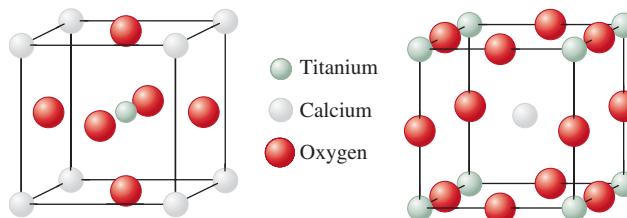
73. The memory metal, nitinol, is an alloy of nickel and titanium. It is called a *memory metal* because after being deformed, a piece of nitinol wire will return to its original shape. The structure of nitinol consists of a simple cubic array of Ni atoms and an inner penetrating simple cubic array of Ti atoms. In the extended lattice, a Ti atom is found at the center of a cube of Ni atoms; the reverse is also true.

- a. Describe the unit cell for nitinol.
- b. What is the empirical formula of nitinol?
- c. What are the coordination numbers (number of nearest neighbors) of Ni and Ti in nitinol?

74. The unit cell for a pure xenon fluoride compound is shown below. What is the formula of the compound?

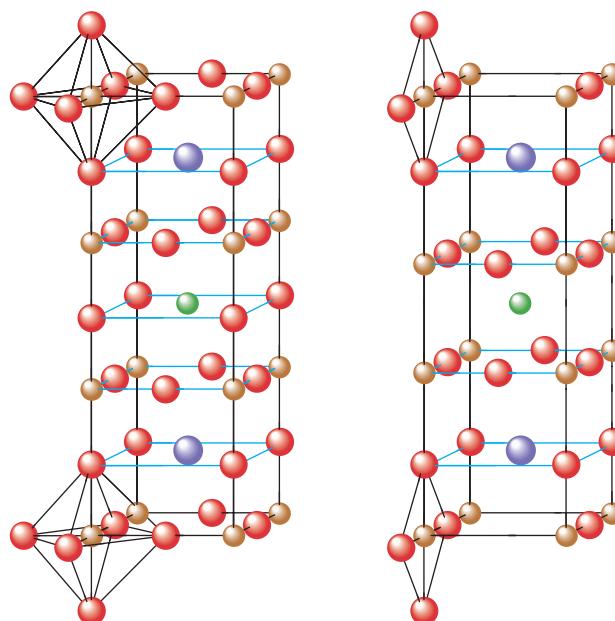


75. Perovskite is a mineral containing calcium, titanium, and oxygen. Two different representations of the unit cell are shown below. Show that both these representations give the same formula and the same number of oxygen atoms around each titanium atom.



76. A mineral crystallizes in a cubic closest packed array of oxygen ions with aluminum ions in some of the octahedral holes and magnesium ions in some of the tetrahedral holes. Deduce the formula of this mineral and predict the fraction of octahedral holes and tetrahedral holes that are filled by the various cations.

77. Materials containing the elements Y, Ba, Cu, and O that are superconductors (electrical resistance equals zero) at temperatures



(a) Ideal perovskite structure

(b) Actual structure of superconductor

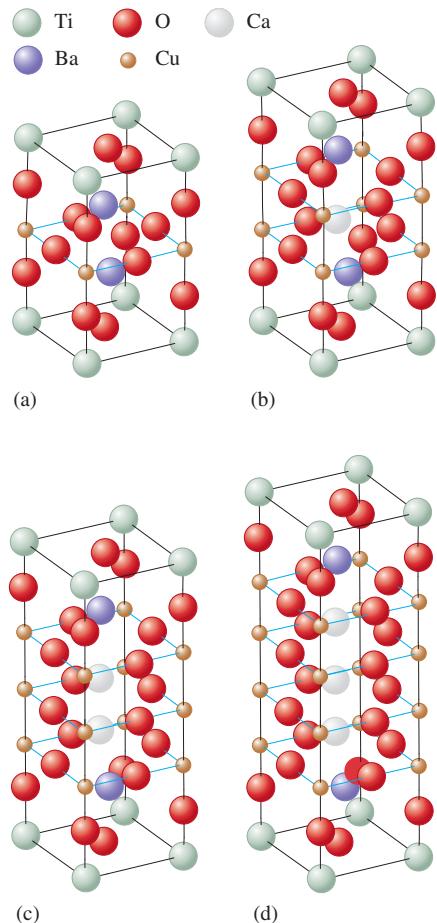
above that of liquid nitrogen were recently discovered. The structures of these materials are based on the perovskite structure. Were they to have the ideal perovskite structure, the superconductor would have the structure shown in part (a) of the figure above.

- What is the formula of this ideal perovskite material?
- How is this structure related to the perovskite structure shown in Exercise 75?

These materials, however, do not act as superconductors unless they are deficient in oxygen. The structure of the actual superconducting phase appears to be that shown in part (b) of the figure.

- What is the formula of this material?
- The structures of another class of ceramic, high-temperature superconductors are shown in the figure below.

- Determine the formula of each of these four superconductors.
- One of the structural features that appears to be essential for high-temperature superconductivity is the presence of planar sheets of copper and oxygen atoms. As the number of sheets in each unit cell increases, the temperature for the onset of superconductivity increases. Order the four structures from lowest to the highest superconducting temperature.
- Assign oxidation states to Cu in each structure assuming Tl exists as Ti^{3+} . The oxidation states of Ca, Ba, and O are assumed to be +2, +2, and -2, respectively.
- It also appears that copper must display a mixture of oxidation states for a material to exhibit superconductivity. Explain how this occurs in these materials as well as in the superconductor in Exercise 77.



Phase Changes and Phase Diagrams

79. 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.

80. 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.

81. In Breckenridge, Colorado, the typical atmospheric pressure is 520. torr. What is the boiling point of water ($\Delta H_{\text{vap}} = 40.7$ kJ/mol) in Breckenridge?

82. What pressure would have to be applied to steam at 350.°C to condense the steam to liquid water ($\Delta H_{\text{vap}} = 40.7$ kJ/mol)?

83. Carbon tetrachloride, CCl_4 , has a vapor pressure of 213 torr at 40.°C and 836 torr at 80.°C. What is the normal boiling point of CCl_4 ?

84. The normal boiling point for acetone is 56.5°C. At an elevation of 5300 ft the atmospheric pressure is 630. torr. What would be the boiling point of acetone ($\Delta H_{\text{vap}} = 32.0$ kJ/mol) at this elevation? What would be the vapor pressure of acetone at 25.0°C at this elevation?

85. A substance, X, has the following properties:

Specific Heat Capacities			
ΔH_{vap}	20. kJ/mol	$C(s)$	3.0 J/g · °C
ΔH_{fus}	5.0 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 substance X starting at -50.°C.

86. Given the data in Exercise 85 on substance X, calculate the energy that must be removed to convert 250. g of substance X from a gas at 100.°C to a solid at -50.°C. Assume X has a molar mass of 75.0 g/mol.

87. How much energy does it take to convert 0.500 kg ice at -20°C to steam at 250°C ? Specific heat capacities: ice, $2.03 \text{ J/g} \cdot ^{\circ}\text{C}$; liquid, $4.2 \text{ J/g} \cdot ^{\circ}\text{C}$; steam, $2.0 \text{ J/g} \cdot ^{\circ}\text{C}$, $\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$, $\Delta H_{\text{fus}} = 6.02 \text{ kJ/mol}$.

88. Consider a 75.0-g sample of $\text{H}_2\text{O}(g)$ at 125°C . What phase or phases are present when 215 kJ of energy is removed from this sample? (See Exercise 87.)

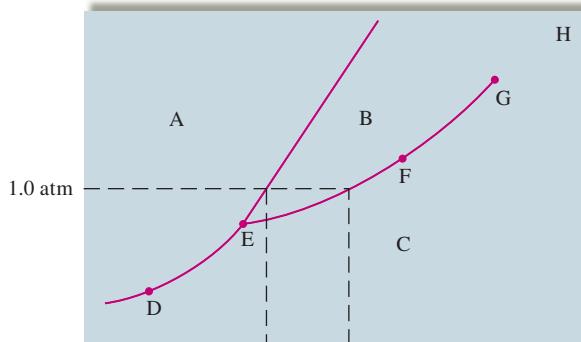
89. An ice cube tray contains enough water at 22.0°C to make 18 ice cubes that each have a mass of 30.0 g. The tray is placed in a freezer that uses CF_2Cl_2 as a refrigerant. The heat of vaporization of CF_2Cl_2 is 158 J/g. What mass of CF_2Cl_2 must be vaporized in the refrigeration cycle to convert all the water at 22.0°C to ice at -5.0°C ? The heat capacities for $\text{H}_2\text{O}(s)$ and $\text{H}_2\text{O}(l)$ are $2.03 \text{ J/g} \cdot ^{\circ}\text{C}$ and $4.18 \text{ J/g} \cdot ^{\circ}\text{C}$, respectively, and the enthalpy of fusion for ice is 6.02 kJ/mol .

90. A 0.250-g chunk of sodium metal is cautiously dropped into a mixture of 50.0 g of water and 50.0 g of ice, both at 0°C . The reaction is

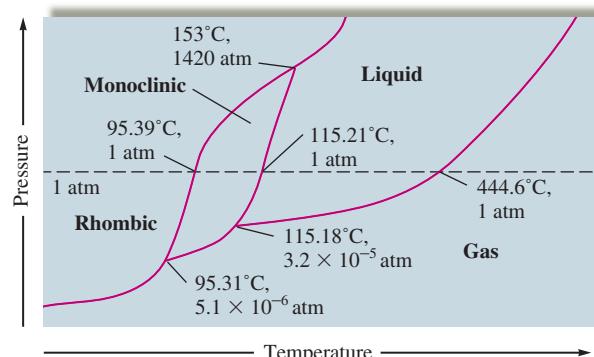


Will the ice melt? Assuming the final mixture has a specific heat capacity of $4.18 \text{ J/g} \cdot ^{\circ}\text{C}$, calculate the final temperature. The enthalpy of fusion for ice is 6.02 kJ/mol .

91. 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. Which phase is denser, solid or liquid?



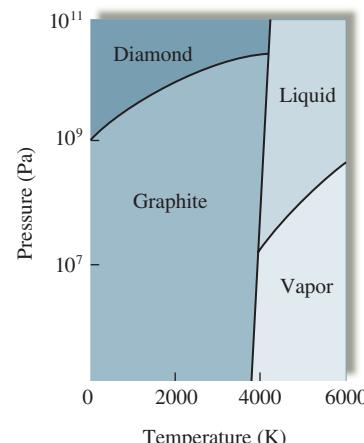
92. Sulfur exhibits two solid phases, rhombic and monoclinic. Use the accompanying phase diagram for sulfur to answer the following questions. (The phase diagram is not to scale.)



- How many triple points are in the phase diagram?
- What phases are in equilibrium at each of the triple points?
- What is the stable phase at 1 atm and 100°C ?
- What are the normal melting point and the normal boiling point of sulfur?
- Which is the densest phase?
- At a pressure of $1.0 \times 10^{-5} \text{ atm}$, can rhombic sulfur sublime?
- What phase changes occur when the pressure on a sample of sulfur at 100°C is increased from $1.0 \times 10^{-8} \text{ atm}$ to 1500 atm ?

93. Use the accompanying phase diagram for carbon to answer the following questions.

- How many triple points are in the phase diagram?
- What phases can coexist at each triple point?
- What happens if graphite is subjected to very high pressures at room temperature?
- If we assume that the density increases with an increase in pressure, which is more dense, graphite or diamond?



94. Like most substances, bromine exists in one of the three typical phases. Br_2 has a normal melting point of -7.2°C and a normal boiling point of 59°C . The triple point for Br_2 is -7.3°C and 40 torr, and the critical point is 320°C and 100 atm. Using this information, sketch a phase diagram for bromine indicating the points described above. Based on your phase diagram, order the three phases from least dense to most dense. What is the stable phase of Br_2 at room temperature and 1 atm? Under what temperature conditions can liquid bromine never exist? What phase changes occur as the temperature of a sample of bromine at 0.10 atm is increased from -50°C to 200°C ?

95. The melting point of a fictional substance X is 225°C at 10.0 atm. If the density of the solid phase of X is 2.67 g/cm^3 and the density of the liquid phase is 2.78 g/cm^3 at 10.0 atm, predict whether the normal melting point of X will be less than, equal to, or greater than 225°C . Explain.

96. Consider the following data for xenon:

Triple point:	-121°C , 280 torr
Normal melting point:	-112°C
Normal boiling point:	-107°C

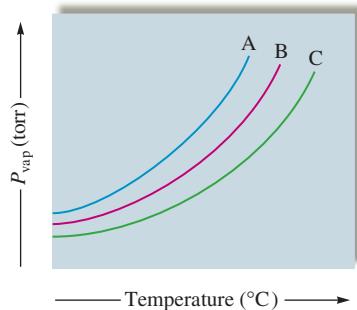
Which is more dense, $\text{Xe}(s)$, or $\text{Xe}(l)$? How do the melting point and boiling point of xenon depend on pressure?

Additional Exercises

97. Rationalize why chalk (calcium carbonate) has a higher melting point than motor oil (large compounds made from carbon and hydrogen), which has a higher melting point than water, which engages in relatively strong hydrogen-bonding interactions.
98. Rationalize the differences in physical properties in terms of intermolecular forces for the following organic compounds. Compare the first three substances with each other, compare the last three with each other, and then compare all six. Can you account for any anomalies?

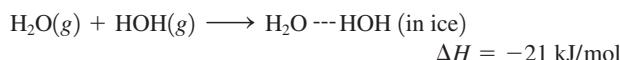
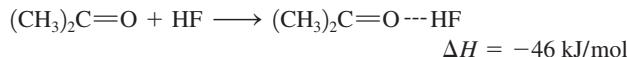
	bp (°C)	mp (°C)	ΔH_{vap} (kJ/mol)
Benzene, C ₆ H ₆	80	6	33.9
Naphthalene, C ₁₀ H ₈	218	80	51.5
Carbon tetrachloride	76	-23	31.8
Acetone, CH ₃ COCH ₃	56	-95	31.8
Acetic acid, CH ₃ CO ₂ H	118	17	39.7
Benzoic acid, C ₆ H ₅ CO ₂ H	249	122	68.2

99. Consider the following vapor pressure versus temperature plot for three different substances A, B, and C.

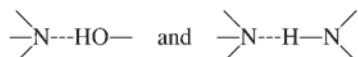


If the three substances are CH₄, SiH₄, and NH₃, match each curve to the correct substance.

100. Consider the following enthalpy changes:



How do the strengths of hydrogen bonds vary with the electronegativity of the element to which hydrogen is bonded? Where in the preceding series would you expect hydrogen bonds of the following type to fall?



101. How could you tell experimentally if TiO₂ is an ionic solid or a network solid?

102. Boron nitride (BN) exists in two forms. The first is a slippery solid formed from the reaction of BCl₃ with NH₃, 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.

103. Consider the following data concerning four different substances.

Compound	Conducts Electricity as a Solid	Other Properties
B ₂ H ₆	no	gas at 25°C
SiO ₂	no	high mp
CsI	no	aqueous solution conducts electricity
W	yes	high mp

Label the four substances as either ionic, network, metallic, or molecular solids.

104. A 20.0-g sample of ice at -10.0°C is mixed with 100.0 g of water at 80.0°C. Calculate the final temperature of the mixture assuming no heat loss to the surroundings. The heat capacities of H₂O(s) and H₂O(l) are 2.03 and 4.18 J/g · °C, respectively, and the enthalpy of fusion for ice is 6.02 kJ/mol.

105. In regions with dry climates, evaporative coolers are used to cool air. A typical electric air conditioner is rated at 1.00×10^4 Btu/h (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 as much heat as a typical electric air conditioner?

106. The critical point of NH₃ is 132°C and 111 atm, and the critical point of N₂ is -147°C and 34 atm. Which of these substances cannot be liquefied at room temperature no matter how much pressure is applied? Explain.

Challenge Problems

107. When 1 mol of benzene is vaporized at a constant pressure of 1.00 atm and its boiling point of 353.0 K, 30.79 kJ of energy (heat) is absorbed and the volume change is +28.90 L. What are ΔE and ΔH for this process?

108. You and a friend each synthesize a compound with the formula XeCl₂F₂. Your compound is a liquid and your friend's compound is a gas (at the same conditions of temperature and pressure). Explain how the two compounds with the same formulas can exist in different phases at the same conditions of pressure and temperature.

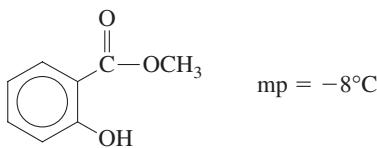
109. Using the heats of fusion and vaporization for water given in Exercise 87, calculate the change in enthalpy for the sublimation of water:



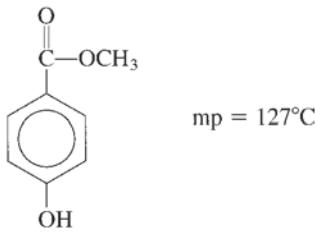
482 Chapter Ten Liquids and Solids

Using the ΔH value given in Exercise 100 and the number of hydrogen bonds formed with each water molecule, estimate what portion of the intermolecular forces in ice can be accounted for by hydrogen bonding.

110. Oil of wintergreen, or methyl salicylate, has the following structure:



Methyl-4-hydroxybenzoate is another molecule with exactly the same molecular formula; it has the following structure:



Account for the large difference in the melting points of the two substances.

111. Consider the following melting point data:

Compound:	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₃	SiCl 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.

112. MnO has either the NaCl type structure or the CsCl type structure (see Exercise 70). The edge length of the MnO unit cell is 4.47×10^{-8} cm and the density of MnO is 5.28 g/cm³.
- Does MnO crystallize in the NaCl or the CsCl type structure?
 - Assuming that the ionic radius of oxygen is 140 pm, estimate the ionic radius of manganese.
113. Some ionic compounds contain a mixture of different charged cations. For example, some titanium oxides contain a mixture of Ti²⁺ and Ti³⁺ ions. Consider a certain oxide of titanium that is 28.31% oxygen by mass and contains a mixture of Ti²⁺ and Ti³⁺ ions. Determine the formula of the compound and the relative numbers of Ti²⁺ and Ti³⁺ ions.
114. Spinel is a mineral that contains 37.9% aluminum, 17.1% magnesium, and 45.0% oxygen, by mass, and has a density of 3.57 g/cm³. The edge of the cubic unit cell measures 809 pm. How many of each type of ion are present in the unit cell?

115. Mn crystallizes in the same type of cubic unit cell as Cu. Assuming that the radius of Mn is 5.6% larger than the radius of Cu and the density of copper is 8.96 g/cm³, calculate the density of Mn.

116. You are asked to help set up a historical display in the park by stacking some cannonballs next to a Revolutionary War cannon. You are told to stack them by starting with a triangle in which each side is composed of four touching cannonballs. You are to continue stacking them until you have a single ball on the top centered over the middle of the triangular base.
- How many cannonballs do you need?
 - What type of closest packing is displayed by the cannonballs?
 - The four corners of the pyramid of cannonballs form the corners of what type of regular geometric solid?

117. 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?

118. The molar enthalpy of vaporization of water at 373 K and 1.00 atm is 40.7 kJ/mol. What fraction of this energy is used to change the internal energy of the water, and what fraction is used to do work against the atmosphere? (*Hint:* Assume that water vapor is an ideal gas.)
119. For a simple cubic array, solve for the volume of an interior sphere (cubic hole) in terms of the radius of a sphere in the array.
120. Consider two different compounds, each with the formula C₂H₆O. One of these compounds is a liquid at room conditions and the other is a gas. Write Lewis structures consistent with this observation and explain your answer. *Hint:* the oxygen atom in both structures satisfies the octet rule with two bonds and two lone pairs.

Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

121. A 0.132-mol sample of an unknown semiconducting material with the formula XY has a mass of 19.0 g. The element X has an electron configuration of [Kr]5s²4d¹⁰. What is this semiconducting material? A small amount of the Y atoms in the semiconductor is replaced with an equivalent amount of atoms with an electron configuration of [Ar]4s²3d¹⁰4p⁵. Does this correspond to n-type or p-type doping?
122. A metal burns in air at 600°C under high pressure to form an oxide with formula MO₂. This compound is 23.72% oxygen by mass. The distance between touching atoms in a cubic closest packed crystal of this metal is 269.0 pm. What is this metal? What is its density?
123. One method of preparing elemental mercury involves roasting cinnabar (HgS) in quicklime (CaO) at 600°C followed by condensation of the mercury vapor. Given the heat of vaporization of mercury (296 J/g) and the vapor pressure of mercury at 25.0°C (2.56×10^{-3} torr), what is the vapor pressure of the condensed mercury at 300°C? How many atoms of mercury are present in the mercury vapor at 300°C if the reaction is conducted in a closed 15.0-L container?

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

124. General Zod has sold Lex Luthor what Zod claims to be a new copper-colored form of kryptonite, the only substance that can harm Superman. Lex, not believing in honor among thieves, decided to carry out some tests on the supposed kryptonite. From previous tests, Lex knew that kryptonite is a metal having a specific heat capacity of $0.082 \text{ J/g} \cdot ^\circ\text{C}$, and a density of 9.2 g/cm^3 .

Lex Luthor's first experiment was an attempt to find the specific heat capacity of kryptonite. He dropped a $10 \text{ g} \pm 3 \text{ g}$ sample of the metal into a boiling water bath at a temperature of $100.0^\circ\text{C} \pm 0.2^\circ\text{C}$. He waited until the metal had reached the bath temperature and then quickly transferred it to $100 \text{ g} \pm 3 \text{ g}$ of water that was contained in a calorimeter at an initial temperature of $25.0^\circ\text{C} \pm 0.2^\circ\text{C}$. The final temperature of the metal and water was 25.2°C . Based on these results, is it possible to distinguish between copper and kryptonite? Explain.

When Lex found that his results from the first experiment were inconclusive, he decided to determine the density of the sample. He managed to steal a better balance and determined the mass of another portion of the purported kryptonite to be $4 \text{ g} \pm 1 \text{ g}$. He dropped this sample into water contained in a 25-mL graduated cylinder and found that it displaced a volume of $0.42 \text{ mL} \pm 0.02 \text{ mL}$. Is the metal copper or kryptonite? Explain.

Lex was finally forced to determine the crystal structure of the metal General Zod had given him. He found that the cubic unit cell contained 4 atoms and had an edge length of 600. pm. Explain how this information enabled Lex to identify the metal as copper or kryptonite.

Will Lex be going after Superman with the kryptonite or seeking revenge on General Zod? What improvements could he have made in his experimental techniques to avoid performing the crystal structure determination?

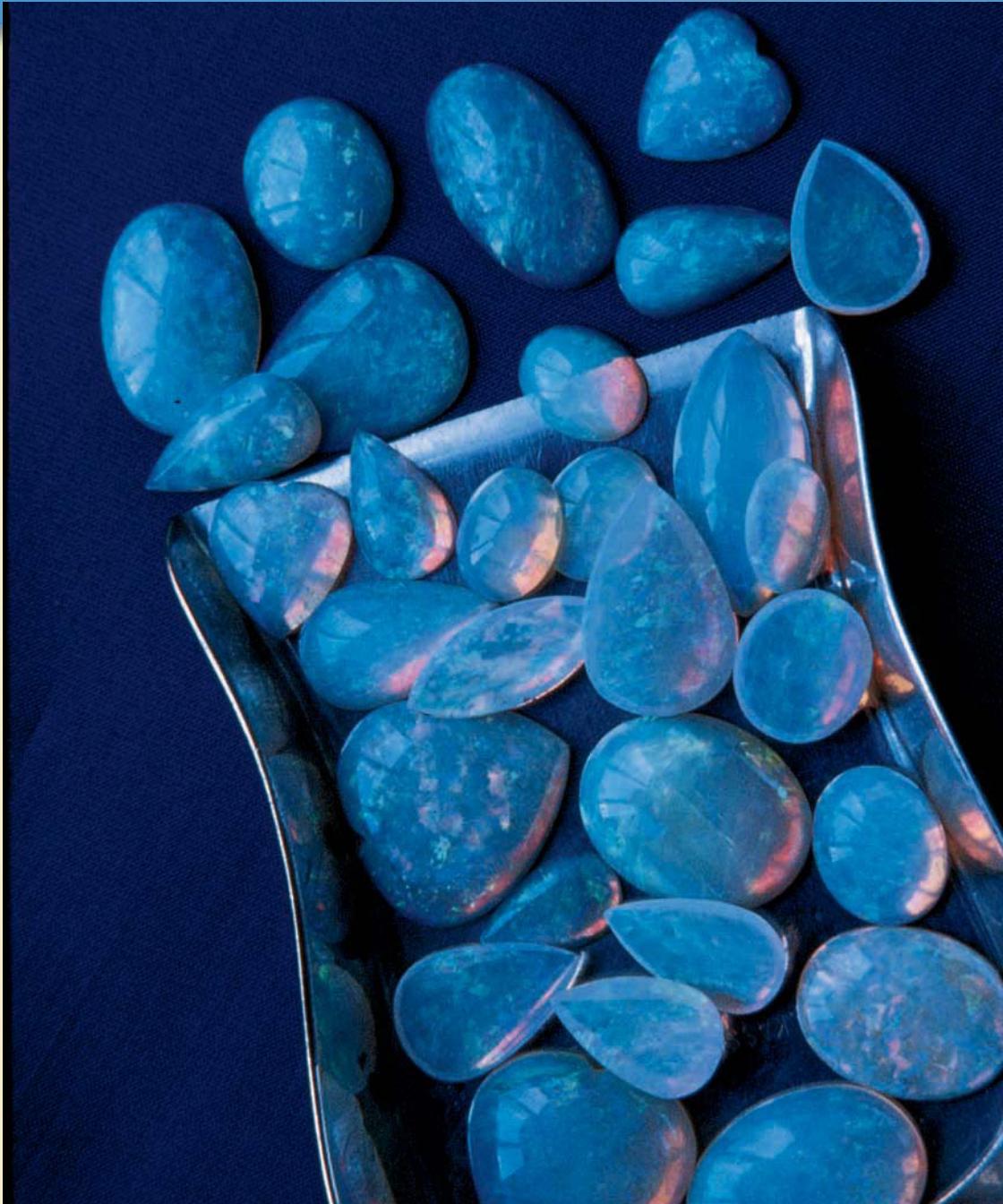


Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmco.com/PIC/zumdahl17e.

11 Properties of Solutions

Contents

- 11.1 Solution Composition
- 11.2 The Energies of Solution Formation
- 11.3 Factors Affecting Solubility
 - Structure Effects
 - Pressure Effects
 - Temperature Effects (for Aqueous Solutions)
- 11.4 The Vapor Pressures of Solutions
 - Nonideal Solutions
- 11.5 Boiling-Point Elevation and Freezing-Point Depression
 - Boiling-Point Elevation
 - Freezing-Point Depression
- 11.6 Osmotic Pressure
 - Reverse Osmosis
- 11.7 Colligative Properties of Electrolyte Solutions
- 11.8 Colloids



Opals are formed from colloidal suspensions of silica when the liquid evaporates.

M

ost of the substances we encounter in daily life are mixtures: Wood, milk, gasoline, champagne, seawater, shampoo, steel, and air are common examples. When the components of a mixture are uniformly intermingled—that is, when a mixture is homogeneous—it is called a *solution*. Solutions can be gases, liquids, or solids, as shown in Table 11.1. However, we will be concerned in this chapter with the properties of liquid solutions, particularly those containing water. As we saw in Chapter 4, many essential chemical reactions occur in aqueous solutions because water is capable of dissolving so many substances.

11.1 Solution Composition

Because a mixture, unlike a chemical compound, has a variable composition, the relative amounts of substances in a solution must be specified. The qualitative terms *dilute* (relatively little solute present) and *concentrated* (relatively large amount of solute) are often used to describe solution content, but we need to define solution composition more precisely to perform calculations. For example, in dealing with the stoichiometry of solution reactions in Chapter 4, we found it useful to describe solution composition in terms of **molarity**, or the number of moles of solute per liter of solution (symbolized by *M*).

Other ways of describing solution composition are also useful. **Mass percent** (sometimes called *weight percent*) is the percent by mass of the solute in the solution:

$$\text{Mass percent} = \left(\frac{\text{mass of solute}}{\text{mass of solution}} \right) \times 100\%$$

Another way of describing solution composition is the **mole fraction** (symbolized by the Greek lowercase letter chi, χ), the ratio of the number of moles of a given component to the total number of moles of solution. For a two-component solution, where n_A and n_B represent the number of moles of the two components,

$$\text{Mole fraction of component A} = \chi_A = \frac{n_A}{n_A + n_B}$$

TABLE 11.1 Various Types of Solutions

Example	State of Solution	State of Solute	State of Solvent
Air, natural gas	Gas	Gas	Gas
Vodka in water, antifreeze	Liquid	Liquid	Liquid
Brass	Solid	Solid	Solid
Carbonated water (soda)	Liquid	Gas	Liquid
Seawater, sugar solution	Liquid	Solid	Liquid
Hydrogen in platinum	Solid	Gas	Solid

A **solute** is the substance being dissolved. The solvent is the dissolving medium.

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

When liquids are mixed, the liquid present in the largest amount is called the **solvent**.

In very dilute aqueous solutions, the magnitude of the molality and the molarity are almost the same.

Still another way of describing solution composition is **molality** (symbolized by m), the number of moles of solute per *kilogram of solvent*:

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilogram of solvent}}$$

Sample Exercise 11.1

Various Methods for Describing Solution Composition

A solution is prepared by mixing 1.00 g ethanol ($\text{C}_2\text{H}_5\text{OH}$) with 100.0 g water to give a final volume of 101 mL. Calculate the molarity, mass percent, mole fraction, and molality of ethanol in this solution.

Solution

Since molarity depends on the volume of the solution, it changes slightly with temperature. Molality is independent of temperature because it depends only on mass.

Molarity: The moles of ethanol can be obtained from its molar mass (46.07 g/mol):

$$1.00 \text{ g C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g C}_2\text{H}_5\text{OH}} = 2.17 \times 10^{-2} \text{ mol C}_2\text{H}_5\text{OH}$$

$$\text{Volume} = 101 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.101 \text{ L}$$

$$\begin{aligned}\text{Molarity of C}_2\text{H}_5\text{OH} &= \frac{\text{moles of C}_2\text{H}_5\text{OH}}{\text{liters of solution}} = \frac{2.17 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} \\ &= 0.215 \text{ M}\end{aligned}$$

Mass percent:

$$\begin{aligned}\text{Mass percent C}_2\text{H}_5\text{OH} &= \left(\frac{\text{mass of C}_2\text{H}_5\text{OH}}{\text{mass of solution}} \right) \times 100\% \\ &= \left(\frac{1.00 \text{ g C}_2\text{H}_5\text{OH}}{100.0 \text{ g H}_2\text{O} + 1.00 \text{ g C}_2\text{H}_5\text{OH}} \right) \times 100\% \\ &= 0.990\% \text{ C}_2\text{H}_5\text{OH}\end{aligned}$$

Mole fraction:

$$\text{Mole fraction of C}_2\text{H}_5\text{OH} = \frac{n_{\text{C}_2\text{H}_5\text{OH}}}{n_{\text{C}_2\text{H}_5\text{OH}} + n_{\text{H}_2\text{O}}}$$

$$n_{\text{H}_2\text{O}} = 100.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} = 5.56 \text{ mol}$$

$$\begin{aligned}\chi_{\text{C}_2\text{H}_5\text{OH}} &= \frac{2.17 \times 10^{-2} \text{ mol}}{2.17 \times 10^{-2} \text{ mol} + 5.56 \text{ mol}} \\ &= \frac{2.17 \times 10^{-2}}{5.58} = 0.00389\end{aligned}$$

Molality:

$$\begin{aligned}\text{Molality of C}_2\text{H}_5\text{OH} &= \frac{\text{moles of C}_2\text{H}_5\text{OH}}{\text{kilogram of H}_2\text{O}} = \frac{2.17 \times 10^{-2} \text{ mol}}{100.0 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}}} \\ &= \frac{2.17 \times 10^{-2} \text{ mol}}{0.1000 \text{ kg}} \\ &= 0.217 \text{ m}\end{aligned}$$

See Exercises 11.25 through 11.27.

TABLE 11.2 The Molar Mass, Equivalent Mass, and Relationship of Molarity and Normality for Several Acids and Bases

Acid or Base	Molar Mass	Equivalent Mass	Relationship of Molarity and Normality
HCl	36.5	36.5	1 M = 1 N
H ₂ SO ₄	98	$\frac{98}{2} = 49$	1 M = 2 N
NaOH	40	40	1 M = 1 N
Ca(OH) ₂	74	$\frac{74}{2} = 37$	1 M = 2 N

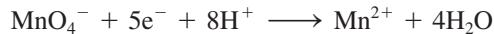
The definition of an equivalent depends on the reaction taking place in the solution.

The quantity we call *equivalent mass* here traditionally has been called *equivalent weight*.

Oxidation-reduction half-reactions were discussed in Section 4.10.

Another concentration measure sometimes encountered is **normality** (symbolized by *N*). Normality is defined as the number of *equivalents* per liter of solution, where the definition of an equivalent depends on the reaction taking place in the solution. For an acid-base reaction, the equivalent is the mass of acid or base that can furnish or accept exactly 1 mole of protons (H⁺ ions). In Table 11.2 note, for example, that the equivalent mass of sulfuric acid is the molar mass divided by 2, since each mole of H₂SO₄ can furnish 2 moles of protons. The equivalent mass of calcium hydroxide is also half the molar mass, since each mole of Ca(OH)₂ contains 2 moles of OH⁻ ions that can react with 2 moles of protons. The equivalent is defined so that 1 equivalent of acid will react with exactly 1 equivalent of base.

For oxidation-reduction reactions, the equivalent is defined as the quantity of oxidizing or reducing agent that can accept or furnish 1 mole of electrons. Thus 1 equivalent of reducing agent will react with exactly 1 equivalent of oxidizing agent. The equivalent mass of an oxidizing or reducing agent can be calculated from the number of electrons in its half-reaction. For example, MnO₄⁻ reacting in acidic solution absorbs five electrons to produce Mn²⁺:

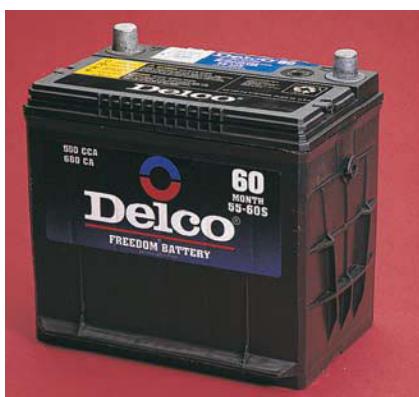


Since the MnO₄⁻ ion present in 1 mole of KMnO₄ consumes 5 moles of electrons, the equivalent mass is the molar mass divided by 5:

$$\text{Equivalent mass of KMnO}_4 = \frac{\text{molar mass}}{5} = \frac{158 \text{ g}}{5} = 31.6 \text{ g}$$

Calculating Various Methods of Solution Composition from the Molarity

Sample Exercise 11.2



A modern 12-volt lead storage battery of the type used in automobiles.

The electrolyte in automobile lead storage batteries is a 3.75 M sulfuric acid solution that has a density of 1.230 g/mL. Calculate the mass percent, molality, and normality of the sulfuric acid.

Solution

The density of the solution in grams per liter is

$$1.230 \frac{\text{g}}{\text{mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 1.230 \times 10^3 \text{ g/L}$$

Thus 1 liter of this solution contains 1230. g of the mixture of sulfuric acid and water. Since the solution is 3.75 M, we know that 3.75 mol H₂SO₄ is present per liter of solution. The number of grams of H₂SO₄ present is

$$3.75 \text{ mol} \times \frac{98.1 \text{ g H}_2\text{SO}_4}{1 \text{ mol}} = 368 \text{ g H}_2\text{SO}_4$$



CHEMICAL IMPACT

Electronic Ink

The printed page has been a primary means of communication for over 3000 years, and researchers at the Massachusetts Institute of Technology (MIT) believe they have discovered why. It seems that the brain responds positively to fixed images on a sheet of paper, particularly those areas of the brain that store and process “spatial maps.” In comparison, information displayed on computer screens or TV screens seems to lack some of the visual signals that stimulate the learning centers of the brain to retain knowledge. While modern technology provides us with many other media by which we can communicate, the appeal of written words on a piece of paper remains. Surprisingly, the technology of printing has changed very little since the invention of the printing press—that is, until now.

In the past several years Joseph M. Jacobson and his students at MIT have developed a prototype of a self-printing

page. The key to this self-printing “paper” is microencapsulation technology—the same technology that is used in “carbonless” carbon paper and “scratch-and-sniff” cologne and perfume advertisements in magazines. Jacobson’s system involves the use of millions of transparent fluid-filled capsules containing microscopic particles. These particles are colored and positively charged on one side and white and negatively charged on the other. When an electric field is selectively applied to the capsules, the white side of the microparticles can be oriented upward or the colored side can be caused to flip up. Appropriate application of an electric field can orient the particles in such a way as to produce words, and once the words have been created, virtually no more energy is needed to keep the particles in place. An image can be maintained on a page with consumption of only 50 millionths of an amp of power! The entire display is about $200\text{ }\mu\text{m}$ thick (2.5 times that of paper)

The amount of water present in 1 liter of solution is obtained from the difference

$$1230.\text{ g solution} - 368\text{ g H}_2\text{SO}_4 = 862\text{ g H}_2\text{O}$$

Since we now know the masses of the solute and solvent, we can calculate the mass percent.

$$\begin{aligned}\text{Mass percent H}_2\text{SO}_4 &= \frac{\text{mass of H}_2\text{SO}_4}{\text{mass of solution}} \times 100\% = \frac{368\text{ g}}{1230.\text{ g}} \times 100\% \\ &= 29.9\% \text{ H}_2\text{SO}_4\end{aligned}$$

From the moles of solute and the mass of solvent we can calculate the molality.

$$\begin{aligned}\text{Molality of H}_2\text{SO}_4 &= \frac{\text{moles H}_2\text{SO}_4}{\text{kilogram of H}_2\text{O}} \\ &= \frac{3.75\text{ mol H}_2\text{SO}_4}{862\text{ g H}_2\text{O} \times \frac{1\text{ kg H}_2\text{O}}{1000\text{ g H}_2\text{O}}} = 4.35\text{ m}\end{aligned}$$

Since each sulfuric acid molecule can furnish two protons, 1 mol H_2SO_4 represents 2 equivalents. Thus a solution with 3.75 mol H_2SO_4 per liter contains $2 \times 3.75 = 7.50$ equivalents per liter, and the normality is 7.50 N.

See Exercise 11.31.

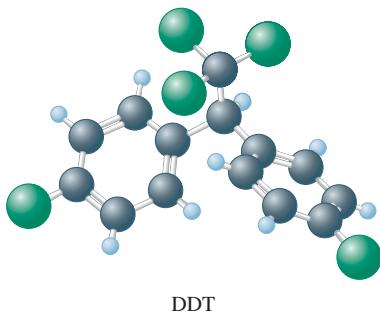
11.2 The Energies of Solution Formation

Dissolving solutes in liquids is very common. We dissolve salt in the water used to cook vegetables, sugar in iced tea, stains in cleaning fluid, gaseous carbon dioxide in water to make soda water, ethanol in gasoline to make gasohol, and so on.

and is so flexible and durable that it can be curled around a pencil and can operate at temperatures from -4 to 158°F . Presently, print resolution is not as good as a modern laser printer, but reduction of the microencapsulated particles from 50 to $40\ \mu\text{m}$ should produce print that rivals the quality of the laser printer.

The first commercial applications of this technology are expected to appear in retail stores across the country in the form of electronic signs that can be updated instantly from a central location. The present technology is a long way from being able to create electronic books, but this is the eventual goal of Jacobson's research team. It seems very likely that this electronic ink technology will contribute greatly to the evolution of the printed page over the next century.

Signs like this one created by E Ink are the first to use electronic ink, which can be updated from a computer inside the store or from a remote location.



Polar solvents dissolve polar solutes; nonpolar solvents dissolve nonpolar solutes.

The enthalpy of solution is the sum of the energies used in expanding both solvent and solute and the energy of solvent-solute interaction.

Solubility is important in other ways. For example, because the pesticide DDT is fat-soluble, it is retained and concentrated in animal tissues, where it causes detrimental effects. This is why DDT, even though it is effective for killing mosquitos, has been banned in the United States. Also, the solubility of various vitamins is important in determining correct dosages. The insolubility of barium sulfate means it can be used safely to improve X rays of the gastrointestinal tract, even though Ba^{2+} ions are quite toxic.

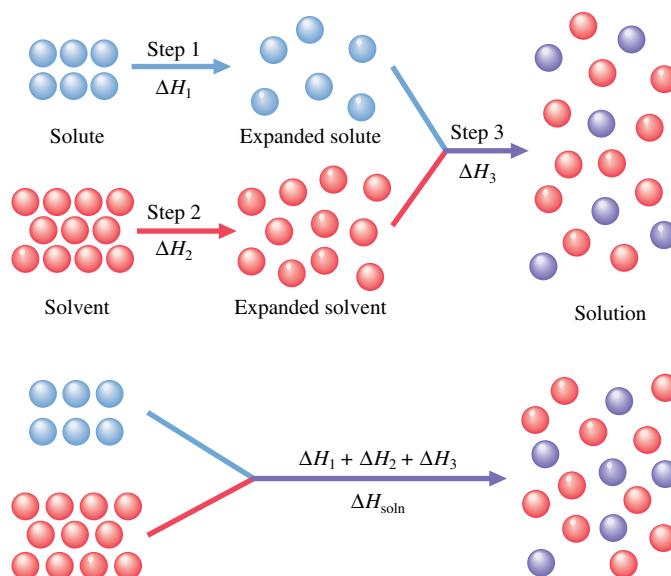
What factors affect solubility? The cardinal rule of solubility is *like dissolves like*. We find that we must use a polar solvent to dissolve a polar or ionic solute and a nonpolar solvent to dissolve a nonpolar solute. Now we will try to understand why this behavior occurs. To simplify the discussion, we will assume that the formation of a liquid solution takes place in three distinct steps.

- **1 Separating the solute into its individual components (expanding the solute).**
- **2 Overcoming intermolecular forces in the solvent to make room for the solute (expanding the solvent).**
- **3 Allowing the solute and solvent to interact to form the solution.**

These steps are illustrated in Fig. 11.1. Steps 1 and 2 require energy, since forces must be overcome to expand the solute and solvent. Step 3 usually releases energy. In other words, steps 1 and 2 are endothermic, and step 3 is often exothermic. The enthalpy change associated with the formation of the solution, called the **enthalpy (heat) of solution (ΔH_{soln})**, is the sum of the ΔH values for the steps:

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

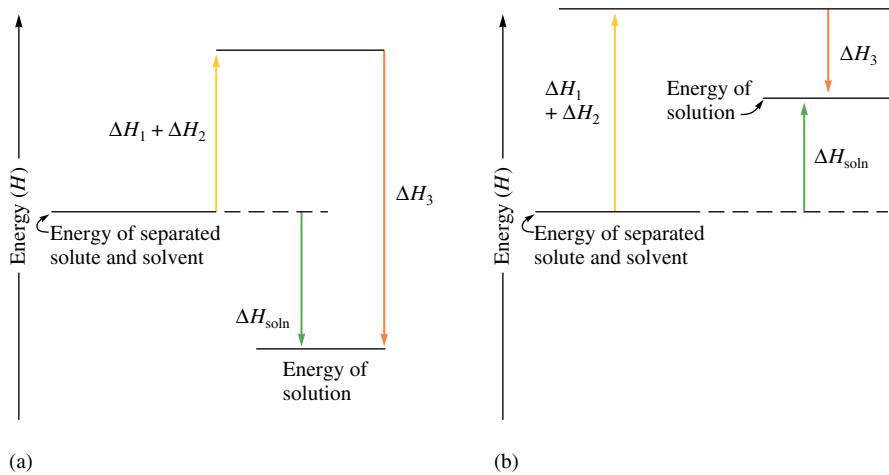
where ΔH_{soln} may have a positive sign (energy absorbed) or a negative sign (energy released), as shown in Fig. 11.2.

**FIGURE 11.1**

The formation of a liquid solution can be divided into three steps: (1) expanding the solute, (2) expanding the solvent, and (3) combining the expanded solute and solvent to form the solution.

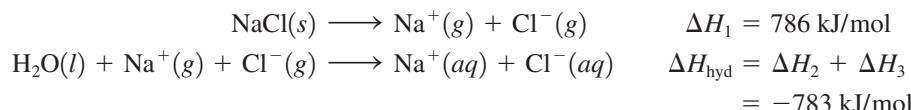
ΔH_1 is expected to be small for nonpolar solutes but can be large for large molecules.

To illustrate the importance of the various energy terms in the equation for ΔH_{soln} , we will consider two specific cases. First, we know that oil is not soluble in water. When oil tankers leak, the petroleum forms an oil slick that floats on the water and is eventually carried onto the beaches. We can explain the immiscibility of oil and water by considering the energy terms involved. Oil is a mixture of nonpolar molecules that interact through London dispersion forces, which depend on molecule size. We expect ΔH_1 to be small for a typical nonpolar solute, but it will be relatively large for the large oil molecules. The term ΔH_3 will be small, since interactions between the nonpolar solute molecules and the polar water molecules will be negligible. However, ΔH_2 will be large and positive because it takes considerable energy to overcome the hydrogen bonding forces among the water molecules to expand the solvent. Thus ΔH_{soln} will be large and positive because of the ΔH_1 and ΔH_2 terms. Since a large amount of energy would have to be expended to form an oil–water solution, this process does not occur to any appreciable extent. These same arguments hold true for any nonpolar solute and polar solvent—the combination of a nonpolar solute and a highly polar solvent is not expected to produce a solution.

**FIGURE 11.2**

The heat of solution (a) ΔH_{soln} has a negative sign (the process is exothermic) if step 3 releases more energy than that required by steps 1 and 2. (b) ΔH_{soln} has a positive sign (the process is endothermic) if steps 1 and 2 require more energy than is released in step 3. (If the energy changes for steps 1 and 2 equal that for step 3, then ΔH_{soln} is zero.)

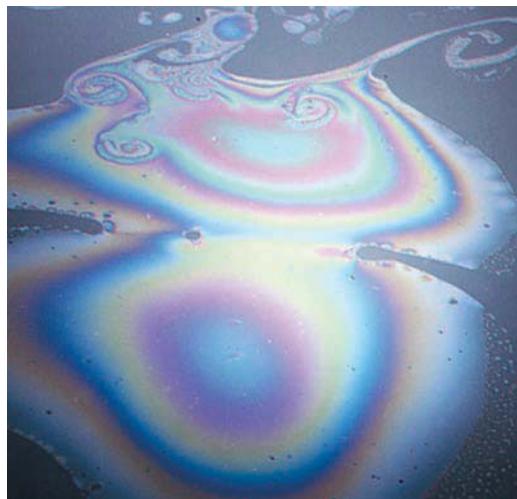
As a second case, let's consider the solubility of an ionic solute, such as sodium chloride, in water. Here the term ΔH_1 is large and positive because the strong ionic forces in the crystal must be overcome, and ΔH_2 is large and positive because hydrogen bonds must be broken in the water. Finally, ΔH_3 is large and negative because of the strong interactions between the ions and the water molecules. In fact, the exothermic and endothermic terms essentially cancel, as shown from the known values:



Here the **enthalpy (heat) of hydration** (ΔH_{hyd}) combines the terms ΔH_2 (for expanding the solvent) and ΔH_3 (for solvent–solute interactions). The heat of hydration represents the enthalpy change associated with the dispersal of a gaseous solute in water. Thus the heat of solution for dissolving sodium chloride is the sum of ΔH_1 and ΔH_{hyd} :

$$\Delta H_{\text{soln}} = 786 \text{ kJ/mol} - 783 \text{ kJ/mol} = 3 \text{ kJ/mol}$$

The factors that act as driving forces for a process are discussed more fully in Chapter 16.



Gasoline floating on water. Since gasoline is nonpolar, it is immiscible with water, because water contains polar molecules.

Note that ΔH_{soln} is small but positive; the dissolving process requires a small amount of energy. Then why is NaCl so soluble in water? The answer lies in nature's tendency toward higher probability of the mixed state. That is, processes naturally run in the direction that leads to the most probable state. For example, imagine equal numbers of orange and yellow spheres separated by a partition, as shown in Fig. 11.3(a). If we remove the partition and shake the container, the spheres will mix [Fig. 11.3(b)], and no amount of shaking will cause them to return to the state of separated orange and yellow. Why? The mixed state is simply much more likely to occur (more probable) than the original separate state because there are many more ways of placing the spheres to give a mixed state than a separated state. This is a general principle. *One factor that favors a process is an increase in probability.*

But energy considerations are also important. *Processes that require large amounts of energy tend not to occur.* Since dissolving 1 mole of solid NaCl requires only a small amount of energy, the solution forms, presumably because of the large increase in the probability of the state when the solute and solvent are mixed.

The various possible cases for solution formation are summarized in Table 11.3. Note that in two cases, polar–polar and nonpolar–nonpolar, the heat of solution is expected to be small. In these cases, the solution forms because of the increase in the probability of the mixed state. In the other cases (polar–nonpolar and nonpolar–polar), the heat of solution is expected to be large and positive, and the large quantity of energy required acts to prevent the solution from forming. Although this discussion has greatly oversimplified the complex driving forces for solubility, these ideas are a useful starting point for understanding the observation that *like dissolves like*.

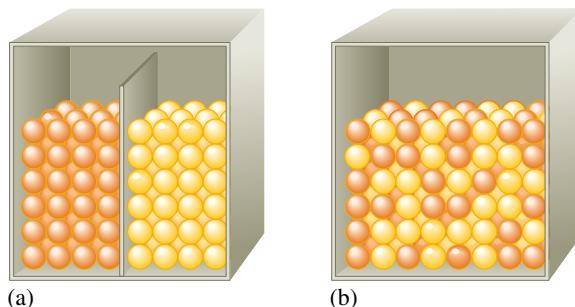


FIGURE 11.3

(a) Orange and yellow spheres separated by a partition in a closed container. (b) The spheres after the partition is removed and the container has been shaken for some time.

TABLE 11.3 The Energy Terms for Various Types of Solutes and Solvents

	ΔH_1	ΔH_2	ΔH_3	ΔH_{soln}	Outcome
Polar solute, polar solvent	Large	Large	Large, negative	Small	Solution forms
Nonpolar solute, polar solvent	Small	Large	Small	Large, positive	No solution forms
Nonpolar solute, nonpolar solvent	Small	Small	Small	Small	Solution forms
Polar solute, nonpolar solvent	Large	Small	Small	Large, positive	No solution forms

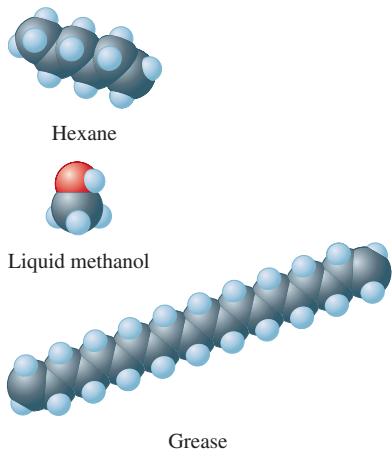
Sample Exercise 11.3**Differentiating Solvent Properties**

Decide whether liquid hexane (C_6H_{14}) or liquid methanol (CH_3OH) is the more appropriate solvent for the substances grease ($C_{20}H_{42}$) and potassium iodide (KI).

Solution

Hexane is a nonpolar solvent because it contains C—H bonds. Thus hexane will work best for the nonpolar solute grease. Methanol has an O—H group that makes it significantly polar. Thus it will serve as the better solvent for the ionic solid KI.

See Exercises 11.37 through 11.39.



11.3 Factors Affecting Solubility

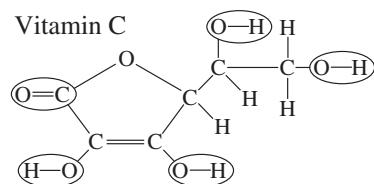
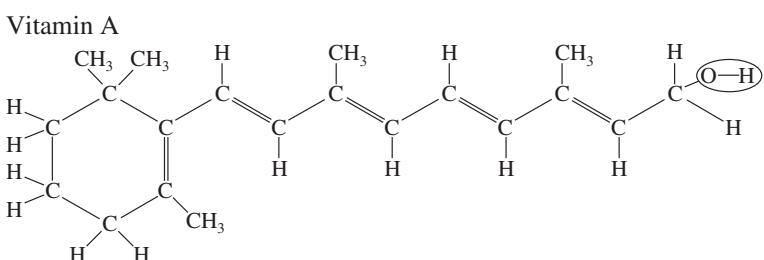
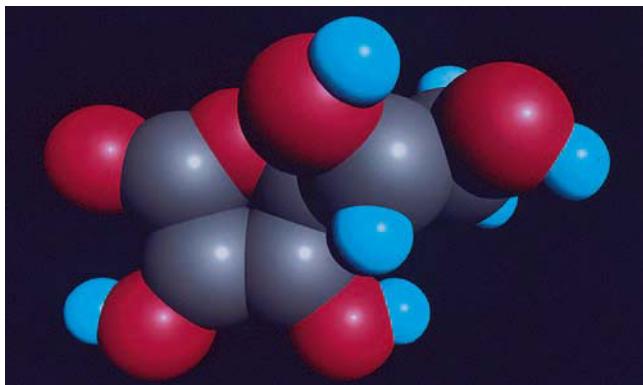
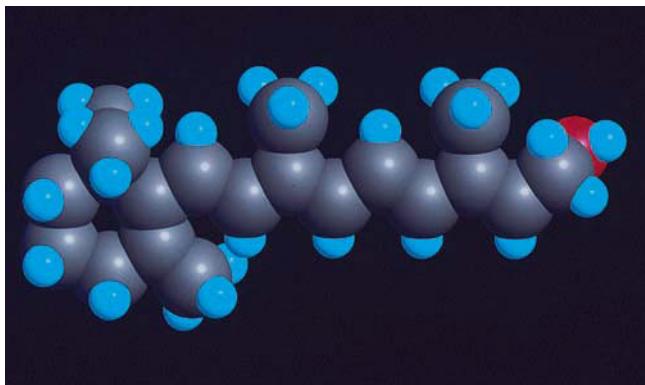
Structure Effects

In the last section we saw that solubility is favored if the solute and solvent have similar polarities. Since it is the molecular structure that determines polarity, there should be a definite connection between structure and solubility. Vitamins provide an excellent example of the relationship among molecular structure, polarity, and solubility.

Recently, there has been considerable publicity about the pros and cons of consuming large quantities of vitamins. For example, large doses of vitamin C have been advocated to combat various illnesses, including the common cold. Vitamin E has been extolled as a youth-preserving elixir and a protector against the carcinogenic (cancer-causing) effects of certain chemicals. However, there are possible detrimental effects from taking large amounts of some vitamins, depending on their solubilities.

Vitamins can be divided into two classes: *fat-soluble* (vitamins A, D, E, and K) and *water-soluble* (vitamins B and C). The reason for the differing solubility characteristics can be seen by comparing the structures of vitamins A and C (Fig. 11.4). Vitamin A, composed mostly of carbon and hydrogen atoms that have similar electronegativities, is virtually nonpolar. This causes it to be soluble in nonpolar materials such as body fat, which is also largely composed of carbon and hydrogen, but not soluble in polar solvents such as water. On the other hand, vitamin C has many polar O—H and C—O bonds, making the molecule polar and thus water-soluble. We often describe nonpolar materials such as vitamin A as *hydrophobic* (water-fearing) and polar substances such as vitamin C as *hydrophilic* (water-loving).

Because of their solubility characteristics, the fat-soluble vitamins can build up in the fatty tissues of the body. This has both positive and negative effects. Since these vitamins

**FIGURE 11.4**

The molecular structures of (a) vitamin A (nonpolar, fat-soluble) and (b) vitamin C (polar, water-soluble). The circles in the structural formulas indicate polar bonds. Note that vitamin C contains far more polar bonds than vitamin A.

can be stored, the body can tolerate for a time a diet deficient in vitamins A, D, E, or K. Conversely, if excessive amounts of these vitamins are consumed, their buildup can lead to the illness *hypervitaminosis*.

In contrast, the water-soluble vitamins are excreted by the body and must be consumed regularly. This fact was first recognized when the British navy discovered that scurvy, a disease often suffered by sailors, could be prevented if the sailors regularly ate fresh limes (which are a good source of vitamin C) when aboard ship (hence the name “limey” for the British sailor).



Carbonation in a bottle of soda.

Pressure Effects

While pressure has little effect on the solubilities of solids or liquids, it does significantly increase the solubility of a gas. Carbonated beverages, for example, are always bottled at high pressures of carbon dioxide to ensure a high concentration of carbon dioxide in the liquid. The fizzing that occurs when you open a can of soda results from the escape of gaseous carbon dioxide because under these conditions the pressure of CO₂ above the solution is now much lower than that used in the bottling process.

The increase in gas solubility with pressure can be understood from Fig. 11.5. Figure 11.5(a) shows a gas in equilibrium with a solution; that is, the gas molecules are entering and leaving the solution at the same rate. If the pressure is suddenly increased [Fig. 11.5(b)], the number of gas molecules per unit volume increases, and the gas enters the solution at a higher rate than it leaves. As the concentration of dissolved gas increases, the rate of the escape of the gas also increases until a new equilibrium is reached [Fig. 11.5(c)], where the solution contains more dissolved gas than before.



CHEMICAL IMPACT

Ionic Liquids?

So far in this text, you have seen that ionic substances are stable solids with high melting points. For example, sodium chloride has a melting point near 800°C. One of the “hottest” areas of current chemical research is ionic liquids—substances composed of ions that are liquids at normal temperatures and pressures. This unusual behavior results from the differences in the sizes of the anions and cations in the ionic liquids. Dozens of small anions, such as BF_4^- (tetrafluoroborate) or PF_6^- (hexafluorophosphate), can be paired with thousands of large cations, such as 1-hexyl-3-methylimidazolium or 1-butyl-3-methylimidazolium (parts a and b respectively, in the accompanying figure). These substances remain liquids because the bulky, asymmetrical cations do not pack together efficiently with the smaller,

symmetrical anions. In contrast, in sodium chloride the ions can pack very efficiently to form a compact, orderly arrangement, leading to maximum cation–anion attractions and thus a high melting point.

The excitement being generated by these ionic liquids arises from many factors. For one thing, almost an infinite variety of ionic liquids are possible due to the large variety of bulky cations and small anions available. According to Kenneth R. Seddon, Director of QUILL (Queen’s University Ionic Liquid Laboratory) in Northern Ireland, a *trillion* ionic liquids are possible. Another great advantage of these liquids is their long liquid range, typically from –100°C to 200°C.

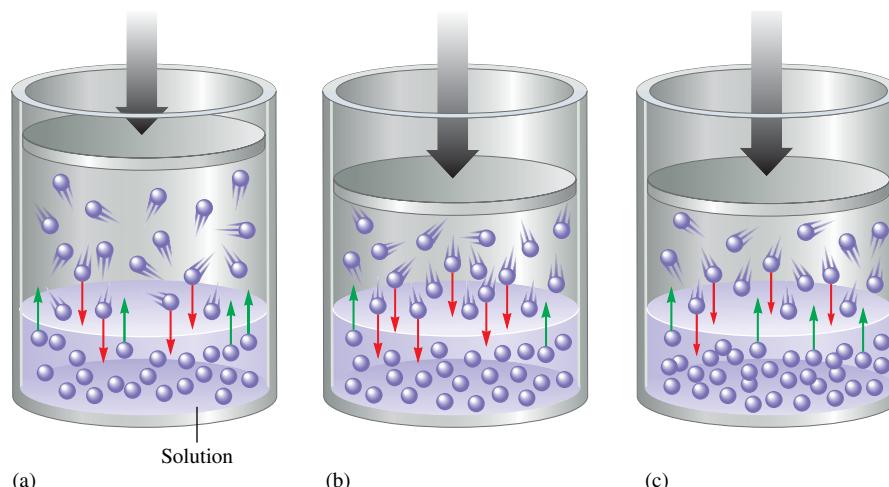
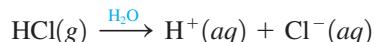
In addition, the cations in the liquids can be designed to perform specific functions. For example, chemist James

The relationship between gas pressure and the concentration of dissolved gas is given by **Henry's law**:

$$C = kP$$

where C represents the concentration of the dissolved gas, k is a constant characteristic of a particular solution, and P represents the partial pressure of the gaseous solute above the solution. In words, Henry's law states that *the amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution*.

Henry's law is obeyed most accurately for dilute solutions of gases that do not dissociate in or react with the solvent. For example, Henry's law is obeyed by oxygen gas in water, but it does *not* correctly represent the behavior of gaseous hydrogen chloride in water because of the dissociation reaction



William Henry (1774–1836), a close friend of John Dalton, formulated his law in 1801.

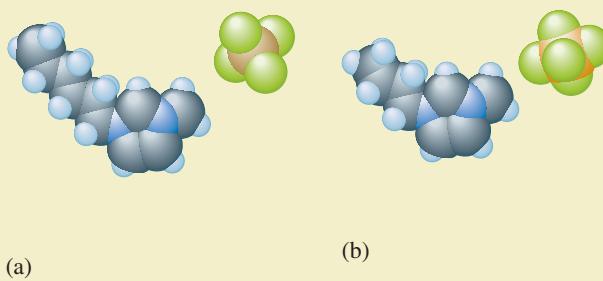
Henry's law holds only when there is no chemical reaction between the solute and solvent.

FIGURE 11.5

(a) A gaseous solute in equilibrium with a solution. (b) The piston is pushed in, which increases the pressure of the gas and the number of gas molecules per unit volume. This causes an increase in the rate at which the gas enters the solution, so the concentration of dissolved gas increases. (c) The greater gas concentration in the solution causes an increase in the rate of escape. A new equilibrium is reached.

H. Davis, of the University of South Alabama in Mobile, has designed various cations that will attract potentially harmful ions such as mercury, cadmium, uranium, and americium (the latter two are commonly found in nuclear waste materials) and leach them out of contaminated solutions. Davis has also developed cations that will remove H₂S (which produces SO₂ when the gas is burned) and CO₂ (which does not burn) from natural gas. Potentially, these ionic solutions might also be used to remove CO₂ from the exhaust gases of fossil-fuel-burning power plants to lessen the “greenhouse effect.”

The biggest obstacle to the widespread use of ionic liquids is their cost. Normal organic solvents used in industry typically cost a few cents per liter, but ionic liquids can cost hundreds of times that amount. However, the environmentally friendly nature of ionic liquids (they produce no vapors because the ions are not volatile) and the flexibility of



these substances as reaction media make them very attractive. As a consequence, efforts are under way to make their use economically feasible.

The term *ionic liquid* may have seemed like an oxymoron in the past, but these substances have a very promising future.

Sample Exercise 11.4

Calculations Using Henry's Law

A certain soft drink is bottled so that a bottle at 25°C contains CO₂ gas at a pressure of 5.0 atm over the liquid. Assuming that the partial pressure of CO₂ in the atmosphere is 4.0×10^{-4} atm, calculate the equilibrium concentrations of CO₂ in the soda both before and after the bottle is opened. The Henry's law constant for CO₂ in aqueous solution is 3.1×10^{-2} mol/L · atm at 25°C.

Solution

We can write Henry's law for CO₂ as

$$C_{\text{CO}_2} = k_{\text{CO}_2} P_{\text{CO}_2}$$

where $k_{\text{CO}_2} = 3.1 \times 10^{-2}$ mol/L · atm. In the *unopened* bottle, $P_{\text{CO}_2} = 5.0$ atm and

$$C_{\text{CO}_2} = k_{\text{CO}_2} P_{\text{CO}_2} = (3.1 \times 10^{-2} \text{ mol/L} \cdot \text{atm})(5.0 \text{ atm}) = 0.16 \text{ mol/L}$$

In the *opened* bottle, the CO₂ in the soda eventually reaches equilibrium with the atmospheric CO₂, so $P_{\text{CO}_2} = 4.0 \times 10^{-4}$ atm and

$$C_{\text{CO}_2} = k_{\text{CO}_2} P_{\text{CO}_2} = \left(3.1 \times 10^{-2} \frac{\text{mol}}{\text{L} \cdot \text{atm}}\right)(4.0 \times 10^{-4} \text{ atm}) = 1.2 \times 10^{-5} \text{ mol/L}$$

Note the large change in concentration of CO₂. This is why soda goes “flat” after being open for a while.

See Exercises 11.43 and 11.44.

Temperature Effects (for Aqueous Solutions)

Everyday experiences of dissolving substances such as sugar may lead you to think that solubility always increases with temperature. This is not the case. The dissolving of a solid occurs *more rapidly* at higher temperatures, but the amount of solid that can be dissolved may increase or decrease with increasing temperature. The effect of temperature

$\Delta H_{\text{soln}}^\circ$ refers to the formation of a 1.0 M ideal solution and is not necessarily relevant to the process of dissolving a solid in a saturated solution. Thus $\Delta H_{\text{soln}}^\circ$ is of limited use in predicting the variation of solubility with temperature.

on the solubility in water of several solids is shown in Fig. 11.6. Note that although the solubility of most solids in water increases with temperature, the solubilities of some substances (such as sodium sulfate and cerium sulfate) decrease with increasing temperature.

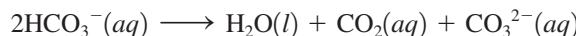
Predicting the temperature dependence of solubility is very difficult. For example, although there is some correlation between the sign of $\Delta H_{\text{soln}}^{\circ}$ and the variation of solubility with temperature, important exceptions exist.* The only sure way to determine the temperature dependence of a solid's solubility is by experiment.

The behavior of gases dissolving in water appears less complex. The solubility of a gas in water typically decreases with increasing temperature,† as is shown for several cases in Fig. 11.7. This temperature effect has important environmental implications because of the widespread use of water from lakes and rivers for industrial cooling. After being used, the water is returned to its natural source at a higher than ambient temperature (**thermal pollution** has occurred). Because it is warmer, this water contains less than the normal concentration of oxygen and is also less dense; it tends to "float" on the colder water below, thus blocking normal oxygen absorption. This effect can be especially important in deep lakes. The warm upper layer can seriously decrease the amount of oxygen available to aquatic life in the deeper layers of the lake.

The decreasing solubility of gases with increasing temperature is also responsible for the formation of *boiler scale*. As we will see in more detail in Chapter 14, the bicarbonate ion is formed when carbon dioxide is dissolved in water containing the carbonate ion:



When the water also contains Ca^{2+} ions, this reaction is especially important—calcium bicarbonate is soluble in water, but calcium carbonate is insoluble. When the water is heated, the carbon dioxide is driven off. For the system to replace the lost carbon dioxide, the reverse reaction must occur:



This reaction, however, also increases the concentration of carbonate ions, causing solid calcium carbonate to form. This solid is the boiler scale that coats the walls of containers such as industrial boilers and tea kettles. Boiler scale reduces the efficiency of heat transfer and can lead to blockage of pipes (see Fig. 11.8).



FIGURE 11.6

The solubilities of several solids as a function of temperature. Note that while most substances become more soluble in water with increasing temperature, sodium sulfate and cerium sulfate become less soluble.

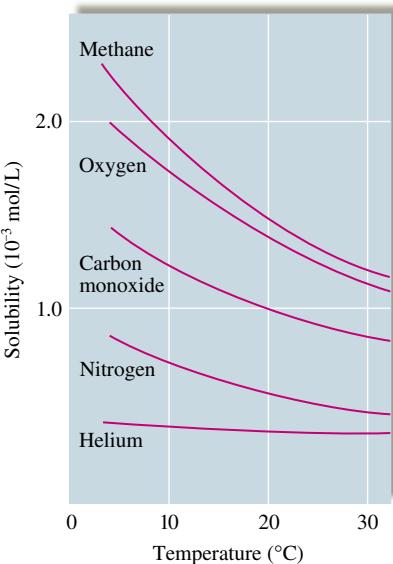


FIGURE 11.7

The solubilities of several gases in water as a function of temperature at a constant pressure of 1 atm of gas above the solution.

*For more information see R. S. Treptow, "Le Châtelier's Principle Applied to the Temperature Dependence of Solubility," *J. Chem. Ed.* **61** (1984): 499.

†The opposite behavior is observed for most nonaqueous solvents.



FIGURE 11.8

A pipe with accumulated mineral deposits. The cross section clearly indicates the reduction in pipe capacity.



CHEMICAL IMPACT

The Lake Nyos Tragedy

On August 21, 1986, a cloud of gas suddenly boiled from Lake Nyos in Cameroon, killing nearly 2000 people. Although at first it was speculated that the gas was hydrogen sulfide, it now seems clear it was carbon dioxide. What would cause Lake Nyos to emit this huge, suffocating cloud of CO₂? Although the answer may never be known for certain, many scientists believe that the lake suddenly “turned over,” bringing to the surface water that contained huge quantities of dissolved carbon dioxide. Lake Nyos is a deep lake that is thermally stratified: Layers of warm, less dense water near the surface float on the colder, denser water layers near the lake’s bottom. Under normal conditions the lake stays this way; there is little mixing among the different layers. Scientists believe that over hundreds or thousands of years, carbon dioxide gas had seeped into the cold water at the lake’s bottom and dissolved in great amounts because of the large pressure of CO₂ present (in accordance with Henry’s law). For some reason on August 21, 1986, the lake apparently suffered an overturn, possibly due to wind or to unusual cooling of the lake’s surface by monsoon clouds. This caused water that was greatly supersaturated with CO₂ to reach the surface and release tremendous quantities of gaseous CO₂ that suffocated thousands of humans and animals before they knew what hit them—a tragic, monumental illustration of Henry’s law.



Lake Nyos in Cameroon.

Since 1986 the scientists studying Lake Nyos and nearby Lake Monoun have observed a rapid recharging of the CO₂ levels in the deep waters of these lakes, causing concern that another deadly gas release could occur at any time. Apparently the only way to prevent such a disaster is to pump away the CO₂-charged deep water in the two lakes. Scientists at a conference to study this problem in 1994 recommended such a solution, but it has not yet been funded by Cameroon.

11.4 The Vapor Pressures of Solutions

Liquid solutions have physical properties significantly different from those of the pure solvent, a fact that has great practical importance. For example, we add antifreeze to the water in a car’s cooling system to prevent freezing in winter and boiling in summer. We also melt ice on sidewalks and streets by spreading salt. These preventive measures work because of the solute’s effect on the solvent’s properties.

To explore how a nonvolatile solute affects a solvent, we will consider the experiment represented in Fig. 11.9, in which a sealed container encloses a beaker containing an aqueous sulfuric acid solution and a beaker containing pure water. Gradually, the volume of the sulfuric acid solution increases and the volume of the pure water decreases. Why? We can explain this observation if the vapor pressure of the pure solvent is greater than that of the solution. Under these conditions, the pressure of vapor necessary to achieve equilibrium with the pure solvent is greater than that required to reach equilibrium with the aqueous acid solution. Thus, as the pure solvent emits vapor to attempt to reach equilibrium, the aqueous sulfuric acid solution absorbs vapor to try to lower the vapor pressure toward its equilibrium value. This process results in a net transfer of water from the pure water through the vapor phase to the sulfuric acid solution. The system can reach an equilibrium vapor pressure only when all the water is transferred to the solution. This

A nonvolatile solute has no tendency to escape from solution into the vapor phase.

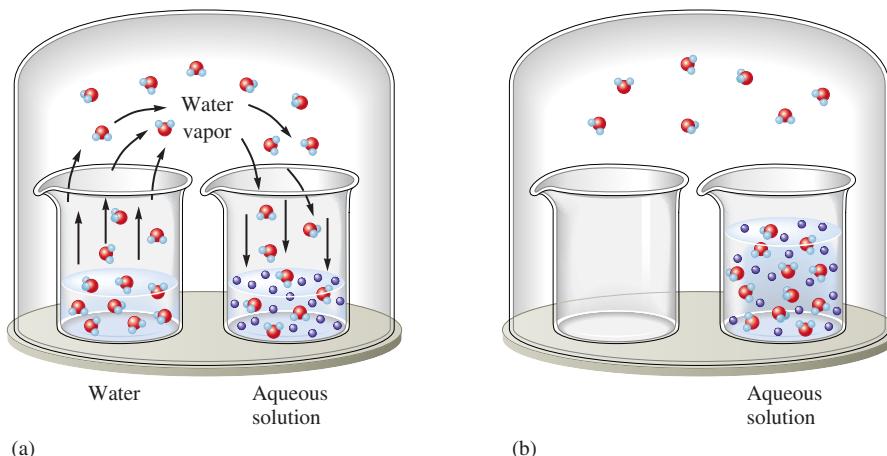


FIGURE 11.9

An aqueous solution and pure water in a closed environment. (a) Initial stage. (b) After a period of time, the water is transferred to the solution.

experiment is just one of many observations indicating that the presence of a *nonvolatile solute lowers the vapor pressure of a solvent*.

We can account for this behavior in terms of the simple model shown in Fig. 11.10. The dissolved nonvolatile solute decreases the number of solvent molecules per unit volume and it should proportionately lower the escaping tendency of the solvent molecules. For example, in a solution consisting of half nonvolatile solute molecules and half solvent molecules, we might expect the observed vapor pressure to be half that of the pure solvent, since only half as many molecules can escape. In fact, this is what is observed.

Detailed studies of the vapor pressures of solutions containing nonvolatile solutes were carried out by François M. Raoult (1830–1901). His results are described by the equation known as **Raoult's law**:

$$P_{\text{soln}} = \chi_{\text{solvent}} P_{\text{solvent}}^0$$

where P_{soln} is the observed vapor pressure of the solution, χ_{solvent} is the mole fraction of solvent, and P_{solvent}^0 is the vapor pressure of the pure solvent. Note that for a solution of half solute and half solvent molecules, χ_{solvent} is 0.5, so the vapor pressure of the solution is half that of the pure solvent. On the other hand, for a solution in which three-fourths of the solution molecules are solvent, $\chi_{\text{solvent}} = \frac{3}{4} = 0.75$, and $P_{\text{soln}} = 0.75P_{\text{solvent}}^0$. The idea is that the nonvolatile solute simply dilutes the solvent.

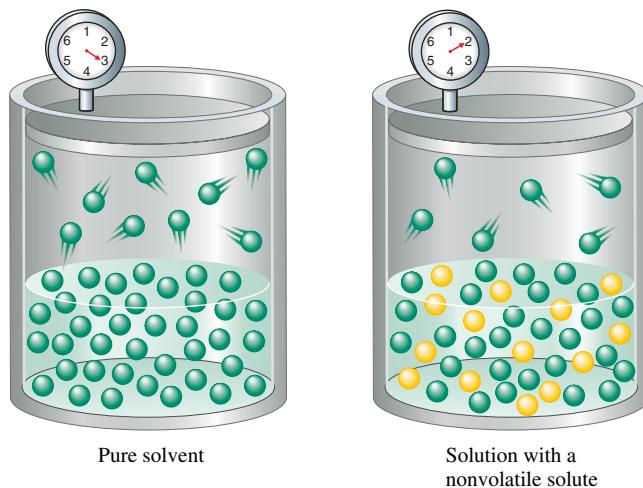


FIGURE 11.10

The presence of a nonvolatile solute inhibits the escape of solvent molecules from the liquid and so lowers the vapor pressure of the solvent.

Raoult's law states that the vapor pressure of a solution is directly proportional to the mole fraction of solvent present.

Sample Exercise 11.5

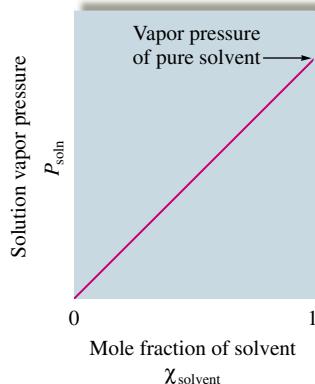


FIGURE 11.11

For a solution that obeys Raoult's law, a plot of P_{soln} versus χ_{solvent} gives a straight line.

Raoult's law is a linear equation of the form $y = mx + b$, where $y = P_{\text{soln}}$, $x = \chi_{\text{solvent}}$, $m = P_{\text{solvent}}^0$, and $b = 0$. Thus a plot of P_{soln} versus χ_{solvent} gives a straight line with a slope equal to P_{solvent}^0 , as shown in Fig. 11.11.

Calculating the Vapor Pressure of a Solution

Calculate the expected vapor pressure at 25°C for a solution prepared by dissolving 158.0 g of common table sugar (sucrose, molar mass = 342.3 g/mol) in 643.5 cm³ of water. At 25°C, the density of water is 0.9971 g/cm³ and the vapor pressure is 23.76 torr.

Solution

We will use Raoult's law in the form

$$P_{\text{soln}} = \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^0$$

To calculate the mole fraction of water in the solution, we must first determine the number of moles of sucrose:

$$\begin{aligned} \text{Moles of sucrose} &= 158.0 \text{ g sucrose} \times \frac{1 \text{ mol sucrose}}{342.3 \text{ g sucrose}} \\ &= 0.4616 \text{ mol sucrose} \end{aligned}$$

To determine the moles of water present, we first convert volume to mass using the density:

$$643.5 \text{ cm}^3 \text{ H}_2\text{O} \times \frac{0.9971 \text{ g H}_2\text{O}}{\text{cm}^3 \text{ H}_2\text{O}} = 641.6 \text{ g H}_2\text{O}$$

The number of moles of water is therefore

$$641.6 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.01 \text{ g H}_2\text{O}} = 35.63 \text{ mol H}_2\text{O}$$

The mole fraction of water in the solution is

$$\begin{aligned} \chi_{\text{H}_2\text{O}} &= \frac{\text{mol H}_2\text{O}}{\text{mol H}_2\text{O} + \text{mol sucrose}} = \frac{35.63 \text{ mol}}{35.63 \text{ mol} + 0.4616 \text{ mol}} \\ &= \frac{35.63 \text{ mol}}{36.09 \text{ mol}} = 0.9873 \end{aligned}$$

Then $P_{\text{soln}} = \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^0 = (0.9873)(23.76 \text{ torr}) = 23.46 \text{ torr}$

Thus the vapor pressure of water has been lowered from 23.76 torr in the pure state to 23.46 torr in the solution. The vapor pressure has been lowered by 0.30 torr.

See Exercises 11.45 and 11.46.

The lowering of vapor pressure depends on the number of solute particles present in the solution.

The phenomenon of the lowering of the vapor pressure gives us a convenient way to “count” molecules and thus provides a means for experimentally determining molar masses. Suppose a certain mass of a compound is dissolved in a solvent and the vapor pressure of the resulting solution is measured. Using Raoult's law, we can determine the number of moles of solute present. Since the mass of this number of moles is known, we can calculate the molar mass.

We also can use vapor pressure measurements to characterize solutions. For example, 1 mole of sodium chloride dissolved in water lowers the vapor pressure approximately twice as much as expected because the solid has two ions per formula unit, which separate when it dissolves. Thus vapor pressure measurements can give valuable information about the nature of the solute after it dissolves.



CHEMICAL IMPACT

Spray Power

Products in aerosol cans are widely used in our society. We use hairsprays, mouth sprays, shaving cream, whipped cream, spray paint, spray cleaners, and many others. As in the case of most consumer products, chemistry plays an important role in making aerosol products work.

An aerosol is a mixture of small particles (solids or liquids) dispersed in some sort of medium (a gas or a liquid). An

inspection of the ingredients in an aerosol can reveals a long list of chemical substances, all of which fall into one of three categories: (1) an active ingredient, (2) an inactive ingredient, or (3) a propellant. The active ingredients perform the functions for which the product was purchased (for example, the resins in hairspray). It is very important that the contents of an aerosol can be chemically compatible. If an undesired chemical reaction were to occur inside the can, it is likely that the product would be unable to perform its function. The inactive ingredients serve to keep the product properly mixed and prevent chemical reactions within the can prior to application. The propellant delivers the product out of the can.

Most aerosol products contain liquefied hydrocarbon propellants* such as propane (C_3H_8) and butane (C_4H_{10}). While these molecules are extremely flammable, they are excellent propellants, and they also help to disperse and mix the components of the aerosol can as they are delivered. These propellants have critical temperatures above room temperature,



Insecticide is sprayed from an aerosol can.

*For foods delivered by aerosol cans, propane and butane are obviously not appropriate propellants. For substances such as whipped cream, the propellant N_2O is often used.

Calculating the Vapor Pressure of a Solution Containing Ionic Solute

Sample Exercise 11.6

Predict the vapor pressure of a solution prepared by mixing 35.0 g solid Na_2SO_4 (molar mass = 142 g/mol) with 175 g water at 25°C. The vapor pressure of pure water at 25°C is 23.76 torr.

Solution

First, we need to know the mole fraction of H_2O .

$$n_{H_2O} = 175 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.0 \text{ g } H_2O} = 9.72 \text{ mol } H_2O$$

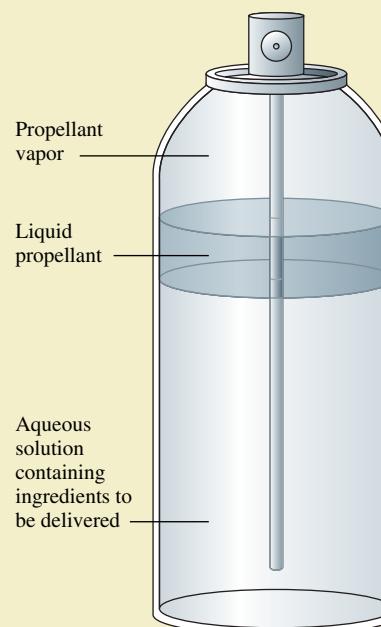
$$n_{Na_2SO_4} = 35.0 \text{ g } Na_2SO_4 \times \frac{1 \text{ mol } Na_2SO_4}{142 \text{ g } Na_2SO_4} = 0.246 \text{ mol } Na_2SO_4$$

It is essential to recognize that when 1 mole of solid Na_2SO_4 dissolves, it produces 2 mol Na^+ ions and 1 mol SO_4^{2-} ions. Thus the number of solute particles present in this solution is three times the number of moles of solute dissolved:

$$n_{\text{solute}} = 3(0.246) = 0.738 \text{ mol}$$

$$\chi_{H_2O} = \frac{n_{H_2O}}{n_{\text{solute}} + n_{H_2O}} = \frac{9.72 \text{ mol}}{0.738 \text{ mol} + 9.72 \text{ mol}} = \frac{9.72}{10.458} = 0.929$$

which means that the intermolecular forces among their molecules are strong enough to form a liquid when pressure is applied. In the highly pressurized aerosol can, the liquid phase of the propellant is in equilibrium with the gaseous phase of the propellant in the head space of the can. The ability of the propellant to maintain this equilibrium is the key to how the aerosol can works. All aerosol cans are constructed in a similar way (see accompanying diagram). At the top of the can is a valve (acts to open and seal the can) and an actuator (to open the valve). Pushing the actuator opens the valve, and the propellant gas escapes through a long tube (the dip tube) that extends from the bottom of the can. With the valve open, the propellant, at a greater pressure than the atmosphere, escapes through the dip tube, carrying the active ingredient(s) with it. The rapidly expanding gas propels the contents from the can and in some instances (for example, shaving cream, carpet shampoo) produces a foam. After each use, the remaining propellant in the can reestablishes equilibrium between the liquid and gaseous phases, keeping the pressure constant within the can as long as sufficient propellant remains. The trick is to have the active and inactive ingredients and the propellant run out at the same time. Given the nature of the most common propellants, you can understand the warning about not putting the “empty” cans in a fire.

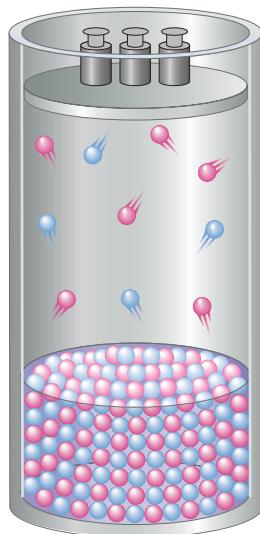


An aerosol can for delivery of an active ingredient dissolved in an aqueous solution.

Now we can use Raoult's law to predict the vapor pressure:

$$P_{\text{soln}} = \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^0 = (0.929)(23.76 \text{ torr}) = 22.1 \text{ torr}$$

See Exercise 11.48.



Nonideal Solutions

So far we have assumed that the solute is nonvolatile and so does not contribute to the vapor pressure over the solution. However, for liquid–liquid solutions where both components are volatile, a modified form of Raoult's law applies:

$$P_{\text{TOTAL}} = P_A + P_B = \chi_A P_A^0 + \chi_B P_B^0$$

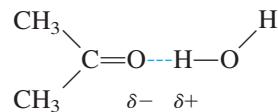
where P_{TOTAL} represents the total vapor pressure of a solution containing A and B, χ_A and χ_B are the mole fractions of A and B, P_A^0 and P_B^0 are the vapor pressures of pure A and pure B, and P_A and P_B are the partial pressures resulting from molecules of A and of B in the vapor above the solution (see Fig. 11.12).

FIGURE 11.12

When a solution contains two volatile components, both contribute to the total vapor pressure. Note that in this case the solution contains equal numbers of the components ● and ○ but the vapor contains more ● than ○. This means that component ● is more volatile (has a higher vapor pressure as a pure liquid) than component ○.

A liquid–liquid solution that obeys Raoult’s law is called an **ideal solution**. Raoult’s law is to solutions what the ideal gas law is to gases. As with gases, ideal behavior for solutions is never perfectly achieved but is sometimes closely approached. Nearly ideal behavior is often observed when the solute–solute, solvent–solvent, and solute–solvent interactions are very similar. That is, in solutions where the solute and solvent are very much alike, the solute simply acts to dilute the solvent. However, if the solvent has a special affinity for the solute, such as if hydrogen bonding occurs, the tendency of the solvent molecules to escape will be lowered more than expected. The observed vapor pressure will be *lower* than the value predicted by Raoult’s law; there will be a *negative deviation from Raoult’s law*.

When a solute and solvent release large quantities of energy in the formation of a solution, that is, when ΔH_{soln} is large and negative, we can assume that strong interactions exist between the solute and solvent. In this case we expect a negative deviation from Raoult’s law, because both components will have a lower escaping tendency in the solution than in the pure liquids. This behavior is illustrated by an acetone–water solution, where the molecules can hydrogen-bond effectively:



Strong solute–solvent interaction gives a vapor pressure lower than that predicted by Raoult’s law.

In contrast, if two liquids mix endothermically, it indicates that the solute–solvent interactions are weaker than the interactions among the molecules in the pure liquids. More energy is required to expand the liquids than is released when the liquids are mixed. In this case the molecules in the solution have a higher tendency to escape than expected, and *positive deviations* from Raoult’s law are observed (see Fig. 11.13). An example of this case is provided by a solution of ethanol and hexane, whose Lewis structures are as follows:

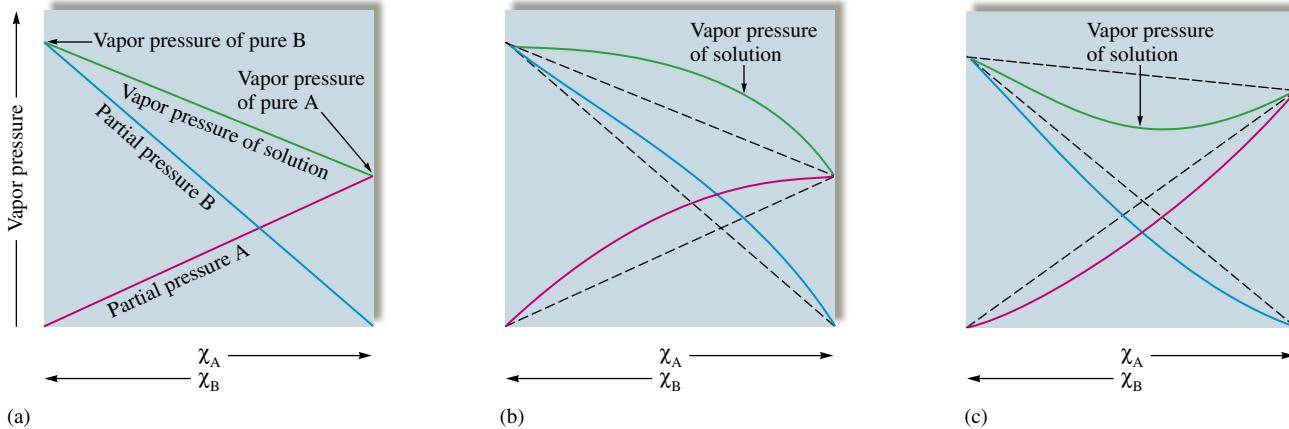
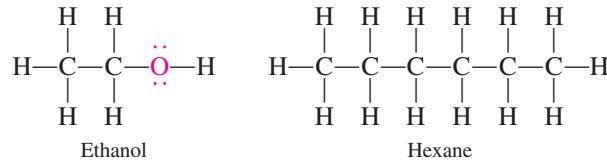
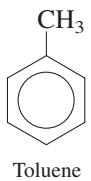


FIGURE 11.13

Vapor pressure for a solution of two volatile liquids. (a) The behavior predicted for an ideal liquid–liquid solution by Raoult’s law. (b) A solution for which P_{TOTAL} is larger than the value calculated from Raoult’s law. This solution shows a positive deviation from Raoult’s law. (c) A solution for which P_{TOTAL} is smaller than the value calculated from Raoult’s law. This solution shows a negative deviation from Raoult’s law.

TABLE 11.4 Summary of the Behavior of Various Types of Solutions

Interactive Forces Between Solute (A) and Solvent (B) Particles	ΔH_{soln}	ΔT for Solution Formation	Deviation from Raoult's Law	Example
$A \leftrightarrow A, B \leftrightarrow B \equiv A \leftrightarrow B$	Zero	Zero	None (ideal solution)	Benzene–toluene
$A \leftrightarrow A, B \leftrightarrow B < A \leftrightarrow B$	Negative (exothermic)	Positive	Negative	Acetone–water
$A \leftrightarrow A, B \leftrightarrow B > A \leftrightarrow B$	Positive (endothermic)	Negative	Positive	Ethanol–hexane



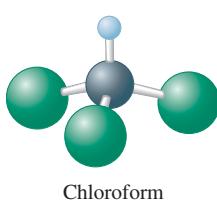
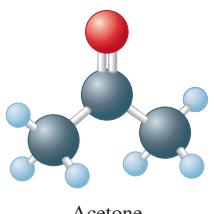
The polar ethanol and the nonpolar hexane molecules are not able to interact effectively. Thus the enthalpy of solution is positive, as is the deviation from Raoult's law.

Finally, for a solution of very similar liquids, such as benzene and toluene (shown in margin), the enthalpy of solution is very close to zero, and thus the solution closely obeys Raoult's law (ideal behavior).

A summary of the behavior of various types of solutions is given in Table 11.4.

Calculating the Vapor Pressure of a Solution Containing Two Liquids

Sample Exercise 11.7



A solution is prepared by mixing 5.81 g acetone (C_3H_6O , molar mass = 58.1 g/mol) and 11.9 g chloroform ($CHCl_3$, molar mass = 119.4 g/mol). At 35°C, this solution has a total vapor pressure of 260. torr. Is this an ideal solution? The vapor pressures of pure acetone and pure chloroform at 35°C are 345 and 293 torr, respectively.

Solution

To decide whether this solution behaves ideally, we first calculate the expected vapor pressure using Raoult's law:

$$P_{\text{TOTAL}} = \chi_A P_A^0 + \chi_C P_C^0$$

where A stands for acetone and C stands for chloroform. The calculated value can then be compared with the observed vapor pressure.

First, we must calculate the number of moles of acetone and chloroform:

$$5.81 \text{ g acetone} \times \frac{1 \text{ mol acetone}}{58.1 \text{ g acetone}} = 0.100 \text{ mol acetone}$$

$$11.9 \text{ g chloroform} \times \frac{1 \text{ mol chloroform}}{119 \text{ g chloroform}} = 0.100 \text{ mol chloroform}$$

Since the solution contains equal numbers of moles of acetone and chloroform, that is,

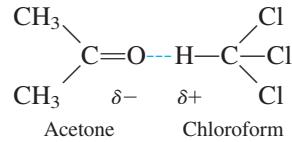
$$\chi_A = 0.500 \quad \text{and} \quad \chi_C = 0.500$$

the expected vapor pressure is

$$P_{\text{TOTAL}} = (0.500)(345 \text{ torr}) + (0.500)(293 \text{ torr}) = 319 \text{ torr}$$

In this case the usually nonpolar C—H bond is strongly polarized by the three attached, highly electronegative chlorine atoms, thus producing hydrogen bonding.

Comparing this value with the observed pressure of 260. torr shows that the solution does not behave ideally. The observed value is lower than that expected. This negative deviation from Raoult's law can be explained in terms of the hydrogen bonding interaction



which lowers the tendency of these molecules to escape from the solution.

See Exercises 11.55 and 11.56.

11.5 Boiling-Point Elevation and Freezing-Point Depression

In the preceding section we saw how a solute affects the vapor pressure of a liquid solvent. Because changes of state depend on vapor pressure, the presence of a solute also affects the freezing point and boiling point of a solvent. Freezing-point depression, boiling-point elevation, and osmotic pressure (discussed in Section 11.6) are called **colligative properties**. As we will see, they are grouped together because they depend only on the number, and not on the identity, of the solute particles in an ideal solution. Because of their direct relationship to the number of solute particles, the colligative properties are very useful for characterizing the nature of a solute after it is dissolved in a solvent and for determining molar masses of substances.

Normal boiling point was defined in Section 10.8.

- Visualization: Boiling-Point Elevation: Liquid/Vapor Equilibrium
- Visualization: Boiling-Point Elevation: Addition of a Solute
- Visualization: Boiling-Point Elevation: Solution/Vapor Equilibrium



Boiling-Point Elevation

The normal boiling point of a liquid occurs at the temperature where the vapor pressure is equal to 1 atmosphere. We have seen that a nonvolatile solute lowers the vapor pressure of the solvent. Therefore, such a solution must be heated to a higher temperature than the boiling point of the pure solvent to reach a vapor pressure of 1 atmosphere. This means that *a nonvolatile solute elevates the boiling point of the solvent*. Figure 11.14 shows the phase diagram for an aqueous solution containing a nonvolatile solute. Note that the liquid/vapor line is shifted to higher temperatures than those for pure water.

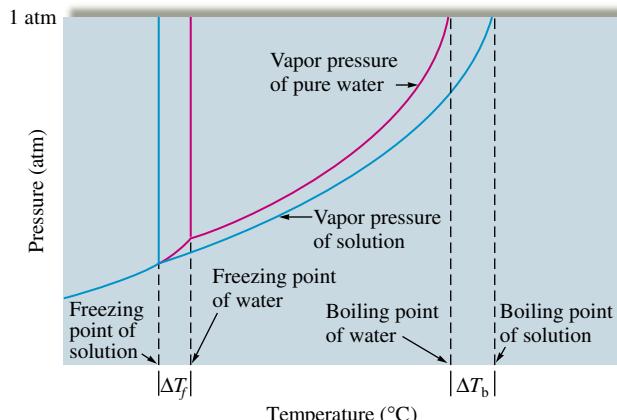


FIGURE 11.14

Phase diagrams for pure water (red lines) and for an aqueous solution containing a nonvolatile solute (blue lines). Note that the boiling point of the solution is higher than that of pure water. Conversely, the freezing point of the solution is lower than that of pure water. The effect of a nonvolatile solute is to extend the liquid range of a solvent.

TABLE 11.5 Molal Boiling-Point Elevation Constants (K_b) and Freezing-Point Depression Constants (K_f) for Several Solvents

Solvent	Boiling Point (°C)	K_b (°C · kg/mol)	Freezing Point (°C)	K_f (°C · kg/mol)
Water (H_2O)	100.0	0.51	0	1.86
Carbon tetrachloride (CCl_4)	76.5	5.03	-22.99	30.
Chloroform ($CHCl_3$)	61.2	3.63	-63.5	4.70
Benzene (C_6H_6)	80.1	2.53	5.5	5.12
Carbon disulfide (CS_2)	46.2	2.34	-111.5	3.83
Ethyl ether ($C_4H_{10}O$)	34.5	2.02	-116.2	1.79
Camphor ($C_{10}H_{16}O$)	208.0	5.95	179.8	40.

As you might expect, the magnitude of the boiling-point elevation depends on the concentration of the solute. The change in boiling point can be represented by the equation

$$\Delta T = K_b m_{\text{solute}}$$

where ΔT is the boiling-point elevation, or the difference between the boiling point of the solution and that of the pure solvent, K_b is a constant that is characteristic of the solvent and is called the **molal boiling-point elevation constant**, and m_{solute} is the *molality* of the solute in the solution.

Values of K_b for some common solvents are given in Table 11.5. The molar mass of a solute can be determined from the observed boiling-point elevation, as shown in Sample Exercise 11.8.

Sample Exercise 11.8

Calculating the Molar Mass by Boiling-Point Elevation

A solution was prepared by dissolving 18.00 g glucose in 150.0 g water. The resulting solution was found to have a boiling point of 100.34°C. Calculate the molar mass of glucose. Glucose is a molecular solid that is present as individual molecules in solution.

Solution

We make use of the equation

$$\Delta T = K_b m_{\text{solute}}$$

where

$$\Delta T = 100.34^\circ\text{C} - 100.00^\circ\text{C} = 0.34^\circ\text{C}$$

From Table 11.5, for water $K_b = 0.51$. The molality of this solution then can be calculated by rearranging the boiling-point elevation equation to give

$$m_{\text{solute}} = \frac{\Delta T}{K_b} = \frac{0.34^\circ\text{C}}{0.51^\circ\text{C} \cdot \text{kg/mol}} = 0.67 \text{ mol/kg}$$

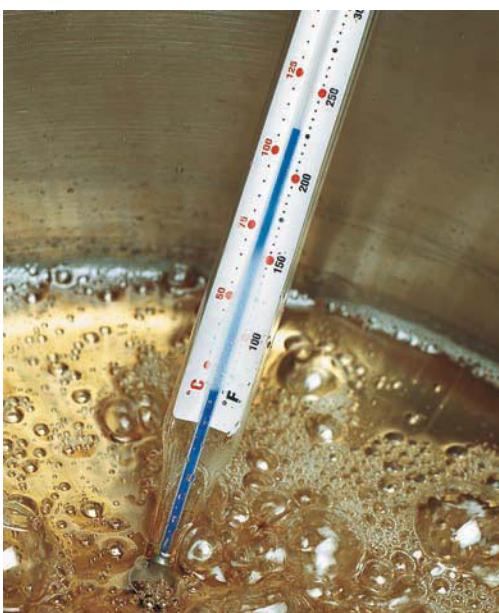
The solution was prepared using 0.1500 kg water. Using the definition of molality, we can find the number of moles of glucose in the solution.

$$m_{\text{solute}} = 0.67 \text{ mol/kg} = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{n_{\text{glucose}}}{0.1500 \text{ kg}}$$

$$n_{\text{glucose}} = (0.67 \text{ mol/kg})(0.1500 \text{ kg}) = 0.10 \text{ mol}$$

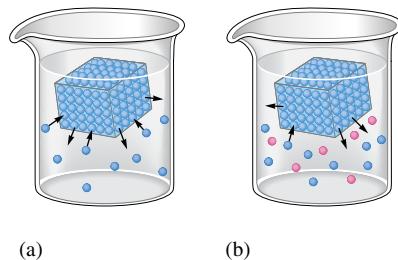
Thus 0.10 mol glucose has a mass of 18.00 g, and 1.0 mol glucose has a mass of 180 g ($10 \times 18.00 \text{ g}$). The molar mass of glucose is 180 g/mol.

See Exercise 11.58.



Sugar dissolved in water to make candy causes the boiling point to be elevated above 100°C.

Melting point and freezing point both refer to the temperature where the solid and liquid coexist.

**FIGURE 11.15**

(a) Ice in equilibrium with liquid water.
(b) Ice in equilibrium with liquid water containing a dissolved solute (shown in pink).

Freezing-Point Depression

When a solute is dissolved in a solvent, the freezing point of the solution is lower than that of the pure solvent. Why? Recall that the vapor pressures of ice and liquid water are the same at 0°C. Suppose a solute is dissolved in water. The resulting solution will not freeze at 0°C because *the water in the solution has a lower vapor pressure than that of pure ice*. No ice will form under these conditions. However, the vapor pressure of ice decreases more rapidly than that of liquid water as the temperature decreases. Therefore, as the solution is cooled, the vapor pressure of the ice and that of the liquid water in the solution will eventually become equal. The temperature at which this occurs is the new freezing point of the solution and is below 0°C. The freezing point has been *depressed*.

We can account for this behavior in terms of the simple model shown in Fig. 11.15. The presence of the solute lowers the rate at which molecules in the liquid return to the solid state. Thus, for an aqueous solution, only the liquid state is found at 0°C. As the solution is cooled, the rate at which water molecules leave the solid ice decreases until this rate and the rate of formation of ice become equal and equilibrium is reached. This is the freezing point of the water in the solution.

Because a solute lowers the freezing point of water, compounds such as sodium chloride and calcium chloride are often spread on streets and sidewalks to prevent ice from forming in freezing weather. Of course, if the outside temperature is lower than the freezing point of the resulting salt solution, ice forms anyway. So this procedure is not effective at extremely cold temperatures.

The solid/liquid line for an aqueous solution is shown on the phase diagram for water in Fig. 11.14. Since the presence of a solute elevates the boiling point and depresses the freezing point of the solvent, adding a solute has the effect of extending the liquid range.

The equation for freezing-point depression is analogous to that for boiling-point elevation:

$$\Delta T = K_f m_{\text{solute}}$$

where ΔT is the freezing-point depression, or the difference between the freezing point of the pure solvent and that of the solution, and K_f is a constant that is characteristic of a particular solvent and is called the **molal freezing-point depression constant**. Values of K_f for common solvents are listed in Table 11.5.

Like the boiling-point elevation, the observed freezing-point depression can be used to determine molar masses and to characterize solutions.

Sample Exercise 11.9

Freezing-Point Depression

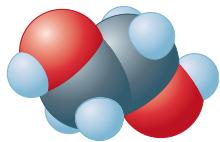
What mass of ethylene glycol ($C_2H_6O_2$, molar mass = 62.1 g/mol), the main component of antifreeze, must be added to 10.0 L of water to produce a solution for use in a car's radiator that freezes at -10.0°F (-23.3°C)? Assume the density of water is exactly 1 g/mL.



- Visualization: Freezing-Point Depression: Solid/Liquid Equilibrium
- Visualization: Freezing-Point Depression: Addition of a Solute
- Visualization: Freezing-Point Depression: Solid/Solution Equilibrium



Spreading salt on a highway.



Ethylene glycol



The addition of antifreeze lowers the freezing point of water in a car's radiator.

Solution

The freezing point must be lowered from 0°C to -23.3°C . To determine the molality of ethylene glycol needed to accomplish this, we can use the equation

$$\Delta T = K_f m_{\text{solute}}$$

where $\Delta T = 23.3^\circ\text{C}$ and $K_f = 1.86$ (from Table 11.5). Solving for the molality gives

$$m_{\text{solute}} = \frac{\Delta T}{K_f} = \frac{23.3^\circ\text{C}}{1.86^\circ\text{C} \cdot \text{kg/mol}} = 12.5 \text{ mol/kg}$$

This means that 12.5 mol ethylene glycol must be added per kilogram of water. We have 10.0 L, or 10.0 kg, of water. Therefore, the total number of moles of ethylene glycol needed is

$$\frac{12.5 \text{ mol}}{\text{kg}} \times 10.0 \text{ kg} = 1.25 \times 10^2 \text{ mol}$$

The mass of ethylene glycol needed is

$$1.25 \times 10^2 \text{ mol} \times \frac{62.1 \text{ g}}{\text{mol}} = 7.76 \times 10^3 \text{ g} (\text{or } 7.76 \text{ kg})$$

See Exercises 11.61 and 11.62.

Sample Exercise 11.10

Determining Molar Mass by Freezing-Point Depression

A chemist is trying to identify a human hormone that controls metabolism by determining its molar mass. A sample weighing 0.546 g was dissolved in 15.0 g benzene, and the freezing-point depression was determined to be 0.240°C . Calculate the molar mass of the hormone.

Solution

From Table 11.5, K_f for benzene is $5.12^\circ\text{C} \cdot \text{kg/mol}$, so the molality of the hormone is

$$m_{\text{hormone}} = \frac{\Delta T}{K_f} = \frac{0.240^\circ\text{C}}{5.12^\circ\text{C} \cdot \text{kg/mol}} = 4.69 \times 10^{-2} \text{ mol/kg}$$

The moles of hormone can be obtained from the definition of molality:

$$4.69 \times 10^{-2} \text{ mol/kg} = m_{\text{solute}} = \frac{\text{mol hormone}}{0.0150 \text{ kg benzene}}$$

or

$$\text{mol hormone} = \left(4.69 \times 10^{-2} \frac{\text{mol}}{\text{kg}}\right)(0.0150 \text{ kg}) = 7.04 \times 10^{-4} \text{ mol}$$

Since 0.546 g hormone was dissolved, 7.04×10^{-4} mol hormone has a mass of 0.546 g, and

$$\frac{0.546 \text{ g}}{7.04 \times 10^{-4} \text{ mol}} = \frac{x \text{ g}}{1.00 \text{ mol}}$$

$$x = 776 \text{ g/mol}$$

Thus the molar mass of the hormone is 776 g/mol.

See Exercises 11.63 and 11.64.



Visualization: Osmosis

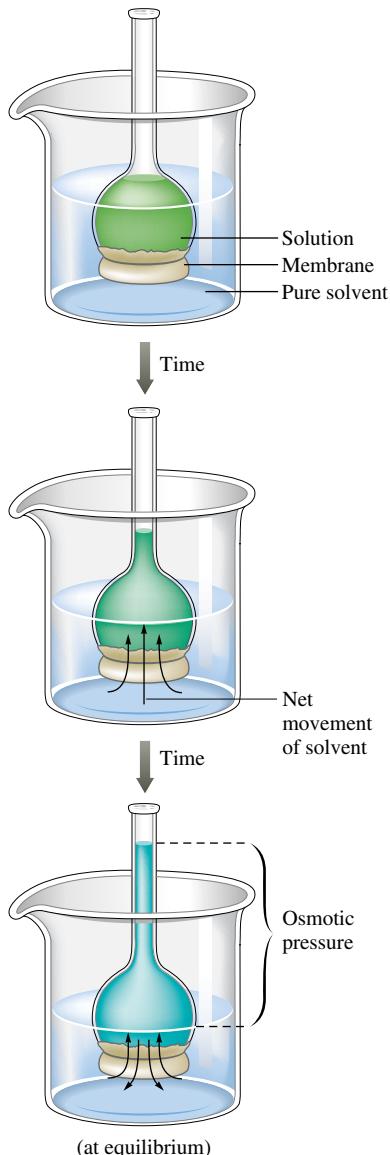


FIGURE 11.16
A tube with a bulb on the end that is covered by a semipermeable membrane. The solution is inside the tube and is bathed in the pure solvent. There is a net transfer of solvent molecules into the solution until the hydrostatic pressure equals the solvent flow in both directions.

11.6 Osmotic Pressure

Osmotic pressure, another of the colligative properties, can be understood from Fig. 11.16. A solution and pure solvent are separated by a **semipermeable membrane**, which allows *solvent but not solute* molecules to pass through. As time passes, the volume of the solution increases and that of the solvent decreases. This flow of solvent into the solution through the semipermeable membrane is called **osmosis**. Eventually the liquid levels stop changing, indicating that the system has reached equilibrium. Because the liquid levels are different at this point, there is a greater hydrostatic pressure on the solution than on the pure solvent. This excess pressure is called the **osmotic pressure**.

We can take another view of this phenomenon, as illustrated in Fig. 11.17. Osmosis can be prevented by applying a pressure to the solution. *The minimum pressure that stops the osmosis is equal to the osmotic pressure of the solution.* A simple model to explain osmotic pressure can be constructed as shown in Fig. 11.18. The membrane allows only solvent molecules to pass through. However, the initial rates of solvent transfer to and from the solution are not the same. The solute particles interfere with the passage of solvent, so the rate of transfer is slower from the solution to the solvent than in the reverse direction. Thus there is a net transfer of solvent molecules into the solution, which causes the solution volume to increase. As the solution level rises in the tube, the resulting pressure exerts an extra “push” on the solvent molecules in the solution, forcing them back through the membrane. Eventually, enough pressure develops so that the solvent transfer becomes equal in both directions. At this point, equilibrium is achieved and the levels stop changing.

Osmotic pressure can be used to characterize solutions and determine molar masses, as can the other colligative properties, but osmotic pressure is particularly useful because a small concentration of solute produces a relatively large osmotic pressure.

Experiments show that the dependence of the osmotic pressure on solution concentration is represented by the equation

$$\Pi = MRT$$

where Π is the osmotic pressure in atmospheres, M is the molarity of the solution, R is the gas law constant, and T is the Kelvin temperature.

A molar mass determination using osmotic pressure is illustrated in Sample Exercise 11.11.

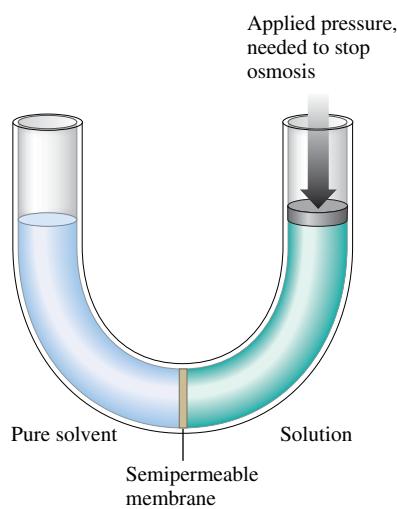
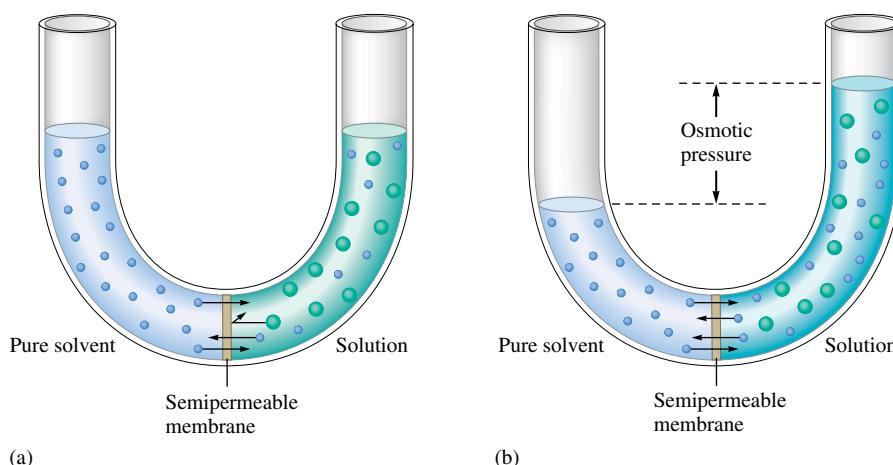


FIGURE 11.17
The normal flow of solvent into the solution (osmosis) can be prevented by applying an external pressure to the solution. The minimum pressure required to stop the osmosis is equal to the osmotic pressure of the solution.

**FIGURE 11.18**

(a) A pure solvent and its solution (containing a nonvolatile solute) are separated by a semipermeable membrane through which solvent molecules (blue) can pass but solute molecules (green) cannot. The rate of solvent transfer is greater from solvent to solution than from solution to solvent. (b) The system at equilibrium, where the rate of solvent transfer is the same in both directions.

Sample Exercise 11.11

Determining Molar Mass from Osmotic Pressure

To determine the molar mass of a certain protein, 1.00×10^{-3} g of it was dissolved in enough water to make 1.00 mL of solution. The osmotic pressure of this solution was found to be 1.12 torr at 25.0°C. Calculate the molar mass of the protein.

Solution

We use the equation

$$\Pi = MRT$$

In this case we have

$$\Pi = 1.12 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.47 \times 10^{-3} \text{ atm}$$

$$R = 0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol}$$

$$T = 25.0 + 273 = 298 \text{ K}$$

Note that the osmotic pressure must be converted to atmospheres because of the units of R .

Solving for M gives

$$M = \frac{1.47 \times 10^{-3} \text{ atm}}{(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})} = 6.01 \times 10^{-5} \text{ mol/L}$$

Since 1.00×10^{-3} g protein was dissolved in 1 mL solution, the mass of protein per liter of solution is 1.00 g. The solution's concentration is 6.01×10^{-5} mol/L. This concentration is produced from 1.00×10^{-3} g protein per milliliter, or 1.00 g/L. Thus 6.01×10^{-5} mol protein has a mass of 1.00 g and

$$\frac{1.00 \text{ g}}{6.01 \times 10^{-5} \text{ mol}} = \frac{x \text{ g}}{1.00 \text{ mol}}$$

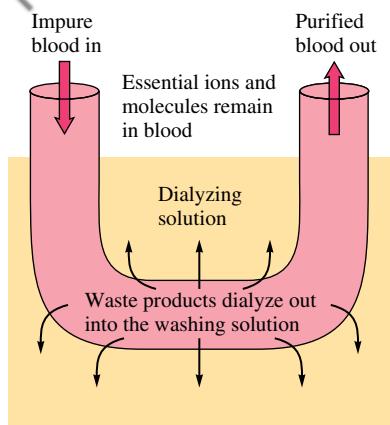
$$x = 1.66 \times 10^4 \text{ g}$$

The molar mass of the protein is 1.66×10^4 g/mol. This molar mass may seem very large, but it is relatively small for a protein.

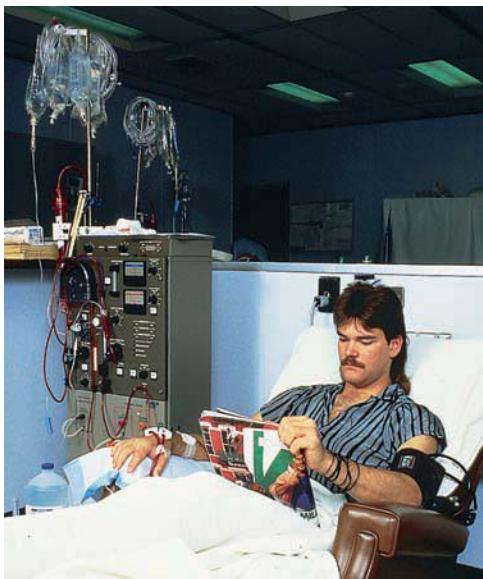
See Exercise 11.66.

Measurements of osmotic pressure generally give much more accurate molar mass values than those from freezing-point or boiling-point changes.

In osmosis, a semipermeable membrane prevents transfer of *all* solute particles. A similar phenomenon, called **dialysis**, occurs at the walls of most plant and animal cells.

**FIGURE 11.19**

Representation of the functioning of an artificial kidney.



Patient undergoing dialysis.

However, in this case the membrane allows transfer of both solvent molecules and *small* solute molecules and ions. One of the most important applications of dialysis is the use of artificial kidney machines to purify the blood. The blood is passed through a cellophane tube, which acts as the semipermeable membrane. The tube is immersed in a dialyzing solution (see Fig. 11.19). This “washing” solution contains the same concentrations of ions and small molecules as blood but has none of the waste products normally removed by the kidneys. The resulting dialysis (movement of waste molecules into the washing solution) cleanses the blood.

Solutions that have identical osmotic pressures are said to be **isotonic solutions**. Fluids administered intravenously must be isotonic with body fluids. For example, if red blood cells are bathed in a hypertonic solution, which is a solution having an osmotic pressure higher than that of the cell fluids, the cells will shrivel because of a net transfer of water out of the cells. This phenomenon is called *crenation*. The opposite phenomenon, called *hemolysis*, occurs when cells are bathed in a hypotonic solution, a solution with an osmotic pressure lower than that of the cell fluids. In this case, the cells rupture because of the flow of water into the cells.

We can use the phenomenon of crenation to our advantage. Food can be preserved by treating its surface with a solute that gives a solution that is hypertonic to bacteria cells. Bacteria on the food then tend to shrivel and die. This is why salt can be used to protect meat and sugar can be used to protect fruit.

The brine used in pickling causes the cucumbers to shrivel.

Sample Exercise 11.12

Isotonic Solutions

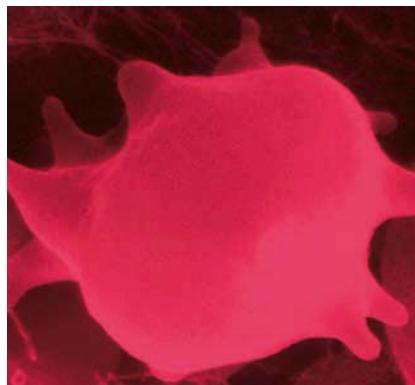
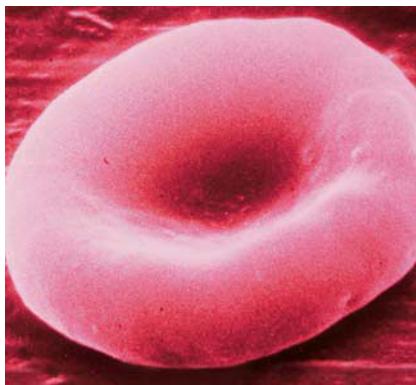
What concentration of sodium chloride in water is needed to produce an aqueous solution isotonic with blood ($\Pi = 7.70 \text{ atm}$ at 25°C)?

Solution

We can calculate the molarity of the solute from the equation

$$\Pi = MRT \quad \text{or} \quad M = \frac{\Pi}{RT}$$

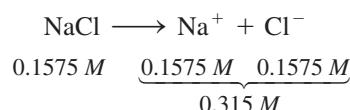
$$M = \frac{7.70 \text{ atm}}{(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})} = 0.315 \text{ mol/L}$$



Red blood cells in three stages of osmosis. (a) The normal shape of a red blood cell. (b) This cell has shrunk because water moved out of it by osmosis. (c) This cell is swollen with water that has moved into it by osmosis.

This represents the total molarity of solute particles. But NaCl gives two ions per formula unit. Therefore, the concentration of NaCl needed is $\frac{0.315\text{ M}}{2} = 0.1575\text{ M} = 0.158\text{ M}$.

That is,



See Exercise 11.68.

Reverse Osmosis

If a solution in contact with pure solvent across a semipermeable membrane is subjected to an external pressure larger than its osmotic pressure, **reverse osmosis** occurs. The pressure will cause a net flow of solvent from the solution to the solvent, as shown in Fig. 11.20. In reverse osmosis, the semipermeable membrane acts as a “molecular filter” to remove solute particles. This fact is applicable to the **desalination** (removal of dissolved salts) of seawater, which is highly hypertonic to body fluids and thus is not drinkable.

As the population of the Sun Belt areas of the United States increases, more demand will be placed on the limited supplies of fresh water there. One obvious source of fresh water is from the desalination of seawater. Various schemes have been suggested, including solar evaporation, reverse osmosis, and even a plan for towing icebergs from Antarctica. The problem, of course, is that all the available processes are expensive. However, as water shortages increase, desalination is becoming necessary. For example, the first full-time public desalination plant in the United States started operations on Catalina Island, just off the coast of California (see Fig. 11.21). This plant, which can produce 132,000 gallons of drinkable water from the Pacific Ocean every day, operates by reverse osmosis. Powerful pumps, developing over 800 lb/in² of pressure, are employed to force seawater through synthetic semipermeable membranes.

Catalina Island's plant may be just the beginning. The city of Santa Barbara opened a \$40 million desalination plant in 1992 that can produce 8 million gallons of drinking water per day, and other plants are in the planning stages.

A small-scale, manually operated reverse osmosis desalinator has been developed by the U.S. Navy to provide fresh water on life rafts. Potable water can be supplied by this desalinator at the rate of 1.25 gallons of water per hour—enough to keep 25 people alive. This compact desalinator, which weighs only 10 pounds, can now replace the bulky cases of fresh water formerly stored in Navy life rafts.

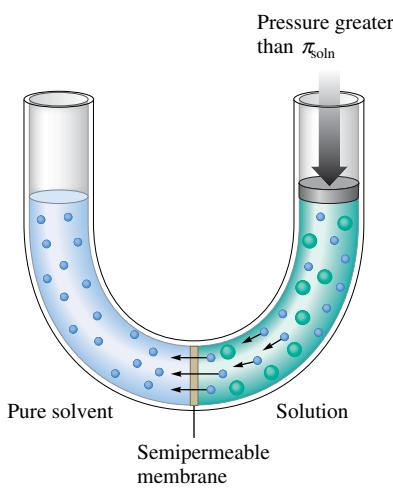
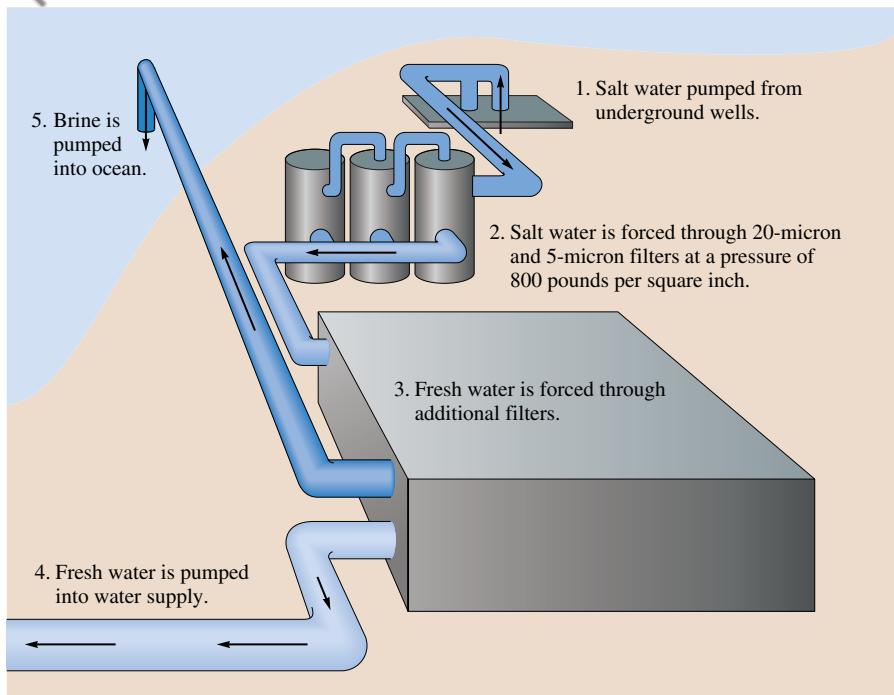


FIGURE 11.20

Reverse osmosis. A pressure greater than the osmotic pressure of the solution is applied, which causes a net flow of solvent molecules (blue) from the solution to the pure solvent. The solute molecules (green) remain behind.



(a)



(b)

FIGURE 11.21

(a) Residents of Catalina Island off the coast of southern California are benefiting from a new desalination plant that can supply 132,000 gallons a day, or one-third of the island's daily needs. (b) Machinery in the desalination plant for Catalina Island.

11.7 Colligative Properties of Electrolyte Solutions

As we have seen previously, the colligative properties of solutions depend on the total concentration of solute particles. For example, a 0.10 m glucose solution shows a freezing point depression of 0.186°C :

$$\Delta T = K_f m = (1.86^\circ\text{C} \cdot \text{kg/mol})(0.100 \text{ mol/kg}) = 0.186^\circ\text{C}$$

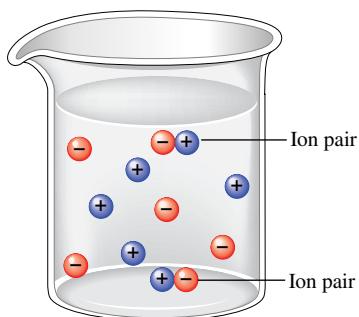
On the other hand, a 0.10 m sodium chloride solution should show a freezing-point depression of 0.37°C , since the solution is 0.10 m Na^+ ions and 0.10 m Cl^- ions. Therefore, the solution contains a total of 0.20 m solute particles, and $\Delta T = (1.86^\circ\text{C} \cdot \text{kg/mol})(0.20 \text{ mol/kg}) = 0.37^\circ\text{C}$.

The relationship between the moles of solute dissolved and the moles of particles in solution is usually expressed using the **van't Hoff factor**, i :

$$i = \frac{\text{moles of particles in solution}}{\text{moles of solute dissolved}}$$

The *expected* value for i can be calculated for a salt by noting the number of ions per formula unit. For example, for NaCl , i is 2; for K_2SO_4 , i is 3; and for $\text{Fe}_3(\text{PO}_4)_2$, i is 5. These calculated values assume that when a salt dissolves, it completely dissociates into its component ions, which then move around independently. This assumption is not always true. For example, the freezing-point depression observed for 0.10 m NaCl is 1.87 times that for 0.10 m glucose rather than twice as great. That is, for a 0.10 m NaCl solution the observed value for i is 1.87 rather than 2. Why? The best explanation is that **ion pairing** occurs in solution (see Fig. 11.22). At a given instant a small percentage of the sodium and chloride ions are paired and thus count as a single particle. In general, ion pairing is most important in concentrated solutions. As the solution becomes more dilute,

Dutch chemist J. H. van't Hoff (1852–1911) received the first Nobel Prize in chemistry in 1901.

**FIGURE 11.22**

In an aqueous solution a few ions aggregate, forming ion pairs that behave as a unit.

TABLE 11.6 Expected and Observed Values of the van't Hoff Factor for 0.05 *m* Solutions of Several Electrolytes

Electrolyte	<i>i</i> (expected)	<i>i</i> (observed)
NaCl	2.0	1.9
MgCl ₂	3.0	2.7
MgSO ₄	2.0	1.3
FeCl ₃	4.0	3.4
HCl	2.0	1.9
Glucose*	1.0	1.0

*A nonelectrolyte shown for comparison.

the ions are farther apart and less ion pairing occurs. For example, in a 0.0010 *m* NaCl solution, the observed value of *i* is 1.97, which is very close to the expected value.

Ion pairing occurs to some extent in all electrolyte solutions. Table 11.6 shows expected and observed values of *i* for a given concentration of various electrolytes. Note that the deviation of *i* from the expected value tends to be greatest where the ions have multiple charges. This is expected because ion pairing ought to be most important for highly charged ions.

The colligative properties of electrolyte solutions are described by including the van't Hoff factor in the appropriate equation. For example, for changes in freezing and boiling points, the modified equation is

$$\Delta T = imK$$

where *K* represents the freezing-point depression or boiling-point elevation constant for the solvent.

For the osmotic pressure of electrolyte solutions, the equation is

$$\Pi = iMRT$$

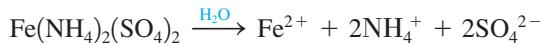
Sample Exercise 11.13

Osmotic Pressure

The observed osmotic pressure for a 0.10 *M* solution of Fe(NH₄)₂(SO₄)₂ at 25°C is 10.8 atm. Compare the expected and experimental values for *i*.

Solution

The ionic solid Fe(NH₄)₂(SO₄)₂ dissociates in water to produce 5 ions:



Thus the expected value for *i* is 5. We can obtain the experimental value for *i* by using the equation for osmotic pressure:

$$\Pi = iMRT \quad \text{or} \quad i = \frac{\Pi}{MRT}$$

where $\Pi = 10.8 \text{ atm}$, $M = 0.10 \text{ mol/L}$, $R = 0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$, and $T = 25 + 273 = 298 \text{ K}$. Substituting these values into the equation gives

$$i = \frac{\Pi}{MRT} = \frac{10.8 \text{ atm}}{(0.10 \text{ mol/L})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 4.4$$

The experimental value for *i* is less than the expected value, presumably because of ion pairing.

See Exercises 11.73 and 11.74.



CHEMICAL IMPACT

The Drink of Champions—Water

In 1965, the University of Florida football team, the Gators, participated in a research program to test a sports drink formula containing a mixture of carbohydrates and electrolytes. The drink was used to help prevent dehydration caused by extreme workouts in the hot Florida climate. The Gators' success that season was in part attributed to their use of the sports drink formula. In 1967, a modified form of this formula was marketed with the name Gatorade. Today, Gatorade leads sales in sports drinks, but many other brands have entered a market where annual sales exceed \$700 million!

During moderate- to high-intensity exercise, glycogen (a fuel reserve that helps maintain normal body processes) can be depleted within 60 to 90 minutes. Blood sugar levels drop as the glycogen reserves are used up, and lactic acid (a by-product of glucose metabolism) builds up in muscle

tissue causing fatigue and muscle cramps. Muscles also generate a large amount of heat that must be dissipated. Water, which has a large specific heat capacity, is used to take heat away from these muscles. Sweating and evaporative cooling help the body maintain a constant temperature, but at a huge cost. During a high-intensity workout in hot weather, anywhere from 1 to 3 quarts of water can be lost from sweating per hour. Sweating away more than 2% of your body weight—a quart for every 100 pounds—can put a large stress on the heart, increasing body temperature and decreasing performance. Excessive sweating also results in the loss of sodium and potassium ions—two very important electrolytes that are present in the fluids inside and outside cells.

All the major sports drinks contain three main ingredients—carbohydrates in the form of simple sugars such as



FIGURE 11.23
The Tyndall effect.

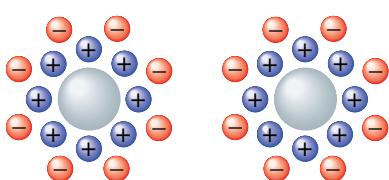


FIGURE 11.24
A representation of two colloidal particles. In each the center particle is surrounded by a layer of positive ions, with negative ions in the outer layer. Thus, although the particles are electrically neutral, they still repel each other because of their outer negative layer of ions.

11.8 Colloids

Mud can be suspended in water by vigorous stirring. When the stirring stops, most of the particles rapidly settle out, but even after several days some of the smallest particles remain suspended. Although undetected in normal lighting, their presence can be demonstrated by shining a beam of intense light through the suspension. The beam is visible from the side because the light is scattered by the suspended particles (Fig. 11.23). In a true solution, on the other hand, the beam is invisible from the side because the individual ions and molecules dispersed in the solution are too small to scatter visible light.

The scattering of light by particles is called the **Tyndall effect** and is often used to distinguish between a suspension and a true solution.

A suspension of tiny particles in some medium is called a **colloidal dispersion**, or a **colloid**. The suspended particles are single large molecules or aggregates of molecules or ions ranging in size from 1 to 1000 nm. Colloids are classified according to the states of the dispersed phase and the dispersing medium. Table 11.7 summarizes various types of colloids.

What stabilizes a colloid? Why do the particles remain suspended rather than forming larger aggregates and precipitating out? The answer is complicated, but the main factor seems to be *electrostatic repulsion*. A colloid, like all other macroscopic substances, is electrically neutral. However, when a colloid is placed in an electric field, the dispersed particles all migrate to the same electrode and thus must all have the same charge. How is this possible? The center of a colloidal particle (a tiny ionic crystal, a group of molecules, or a single large molecule) attracts from the medium a layer of ions, all of the same charge. This group of ions, in turn, attracts another layer of oppositely charged ions, as shown in Fig. 11.24. Because the colloidal particles all have an outer layer of ions with the same charge, they repel each other and do not easily aggregate to form particles that are large enough to precipitate.

sucrose, glucose, and fructose; electrolytes, including sodium and potassium ions; and water. Because these are the three major substances lost through sweating, good scientific reasoning suggests that drinking sports drinks should improve performance. But just how effectively do sports drinks deliver on their promises?

Recent studies have confirmed that athletes who eat a balanced diet and drink plenty of water are just as well off as those who consume sports drinks. A sports drink may have only one advantage over drinking water—it tastes better than water to most athletes. And if a drink tastes better, it will encourage more consumption, thus keeping cells hydrated.

Since most of the leading sports drinks contain the same ingredients in similar concentrations, taste may be the single most important factor in choosing your drink. If you are not interested in any particular sports drink, drink plenty of water. The key to quality performance is to keep your cells hydrated.



For healthy athletes, drinking water during exercise may be as effective as drinking sports drinks.

Adapted with permission from "Sports Drinks: Don't Sweat the Small Stuff," by Tim Graham, *ChemMatters*, February 1999, p. 11.

TABLE 11.7 Types of Colloids

Examples	Dispersing Medium	Dispersed Substance	Colloid Type
Fog, aerosol sprays	Gas	Liquid	Aerosol
Smoke, airborne bacteria	Gas	Solid	Aerosol
Whipped cream, soap suds	Liquid	Gas	Foam
Milk, mayonnaise	Liquid	Liquid	Emulsion
Paint, clays, gelatin	Liquid	Solid	Sol
Marshmallow, polystyrene foam	Solid	Gas	Solid foam
Butter, cheese	Solid	Liquid	Solid emulsion
Ruby glass	Solid	Solid	Solid sol

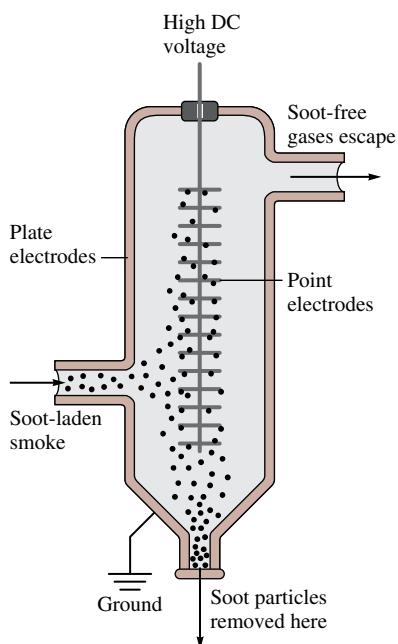


FIGURE 11.25

The Cottrell precipitator installed in a smokestack. The charged plates attract the colloidal particles because of their ion layers and thus remove them from the smoke.

The destruction of a colloid, called **coagulation**, usually can be accomplished either by heating or by adding an electrolyte. Heating increases the velocities of the colloidal particles, causing them to collide with enough energy that the ion barriers are penetrated and the particles can aggregate. Because this process is repeated many times, the particle grows to a point where it settles out. Adding an electrolyte neutralizes the adsorbed ion layers. This is why clay suspended in rivers is deposited where the river reaches the ocean, forming the deltas characteristic of large rivers like the Mississippi. The high salt content of the seawater causes the colloidal clay particles to coagulate.

The removal of soot from smoke is another example of the coagulation of a colloid. When smoke is passed through an electrostatic precipitator (Fig. 11.25), the suspended solids are removed. The use of precipitators has produced an immense improvement in the air quality of heavily industrialized cities.



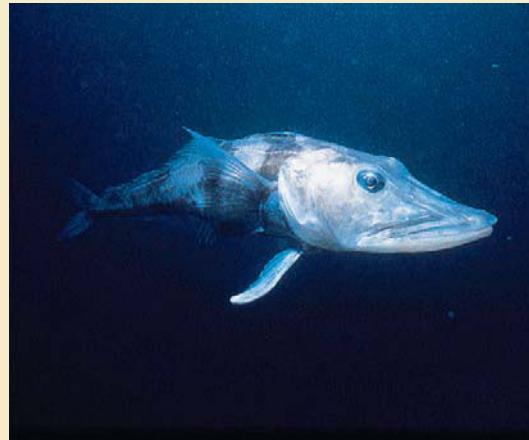
CHEMICAL IMPACT

Organisms and Ice Formation

The ice-cold waters of the polar oceans are teeming with fish that seem immune to freezing. One might think that these fish have some kind of antifreeze in their blood. However, studies show that they are protected from freezing in a very different way from the way antifreeze protects our cars. As we have seen in this chapter, solutes such as sugar, salt, and ethylene glycol lower the temperature at which the solid and liquid phases of water can coexist. However, the fish could not tolerate high concentrations of solutes in their blood because of the osmotic pressure effects. Instead, they are protected by proteins in their blood. These proteins allow the water in the bloodstream to be supercooled—exist below 0°C—without forming ice. They apparently coat the surface of each tiny ice crystal, as soon as it begins to form, preventing it from growing to a size that would cause biological damage.

Although it might at first seem surprising, this research on polar fish has attracted the attention of ice cream manufacturers. Premium quality ice cream is smooth; it does not have large ice crystals in it. The makers of ice cream would like to incorporate these polar fish proteins, or molecules that behave similarly, into ice cream to prevent the growth of ice crystals during storage.

Fruit and vegetable growers have a similar interest: They also want to prevent ice formation that damages their crops during an unusual cold wave. However, this is a very different kind of problem than keeping polar fish from freezing. Many types of fruits and vegetables are colonized by



An Antarctic fish, *Chaerophalus aceratus*.

bacteria that manufacture a protein that *encourages* freezing by acting as a nucleating agent to start an ice crystal. Chemists have identified the offending protein in the bacteria and the gene that is responsible for making it. They have learned to modify the genetic material of these bacteria in a way that removes their ability to make the protein that encourages ice crystal formation. If testing shows that these modified bacteria have no harmful effects on the crop or the environment, the original bacteria strain will be replaced with the new form so that ice crystals will not form so readily when a cold snap occurs.

Key Terms

Section 11.1

molarity
mass percent
mole fraction
molality
normality

Section 11.2

enthalpy (heat) of solution
enthalpy (heat) of hydration

Section 11.3

Henry's law
thermal pollution

Section 11.4

Raoult's law
ideal solution

For Review

Solution composition

- Molarity (M): moles solute per liter of solution
- Mass percent: ratio of mass of solute to mass of solution times 100%
- Mole fraction (χ): ratio of moles of a given component to total moles of all components
- Molality (m): moles solute per mass of solvent (in kg)
- Normality (N): number of equivalents per liter of solution

Enthalpy of solution (ΔH_{soln})

- The enthalpy change accompanying solution formation
- Can be partitioned into
 - The energy required to overcome the solute–solute interactions
 - The energy required to “make holes” in the solvent
 - The energy associated with solute–solvent interactions

Section 11.5

colligative properties
molal boiling-point elevation constant
molal freezing-point depression constant

Section 11.6

semipermeable membrane
osmosis
osmotic pressure
dialysis
isotonic solution
reverse osmosis
desalination

Section 11.7

van't Hoff factor
ion pairing

Section 11.8

Tyndall effect
colloid (colloidal dispersion)
coagulation

Factors That Affect Solubility

- Polarity of solute and solvent
 - “Like dissolves like” is a useful generalization
- Pressure increases the solubility of gases in a solvent
 - Henry’s law: $C = kP$
- Temperature effects
 - Increased temperature decreases the solubility of a gas in water
 - Most solids are more soluble at higher temperatures but important exceptions exist

Vapor Pressure of Solutions

- A solution containing a nonvolatile solute has a lower vapor pressure than a solution of the pure solvent
- Raoult’s law defines an ideal solution

$$P_{\text{vapor}}^{\text{soln}} = \chi_{\text{solvent}} P_{\text{vapor}}^{\text{solvent}}$$

- Solutions in which the solute–solvent attractions differ from the solute–solute and solvent–solvent attractions violate Raoult’s law

Colligative Properties

- Depend on the number of solute particles present
- Boiling-point elevation: $\Delta T = K_b m_{\text{solute}}$
- Freezing-point lowering: $\Delta T = K_f m_{\text{solute}}$
- Osmotic pressure: $\Pi = MRT$
 - Osmosis occurs when a solution and pure solvent are separated by a semipermeable membrane that allows solvent molecules to pass but not solute particles
 - Reverse osmosis occurs when the applied pressure is greater than the osmotic pressure of the solution
- Because colligative properties depend on the number of particles, solutes that break into several ions when they dissolve have an effect proportional to the number of ions produced
 - The van’t Hoff factor i represents the number of ions produced by each formula unit of solute

Colloids

- A suspension of tiny particles stabilized by electrostatic repulsion among the ion layers surrounding the individual particles
- Can be coagulated (destroyed) by heating or adding an electrolyte

REVIEW QUESTIONS

- The four most common ways to describe solution composition are mass percent, mole fraction, molarity, and molality. Define each of these solution composition terms. Why is molarity temperature-dependent, whereas the other three solution composition terms are temperature-independent?
- Using KF as an example, write equations that refer to ΔH_{soln} and ΔH_{hyd} . Lattice energy was defined in Chapter 8 as ΔH for the reaction $\text{K}^+(g) + \text{F}^-(g) \longrightarrow \text{KF}(s)$. Show how you would utilize Hess’s law to calculate ΔH_{soln} from ΔH_{hyd} and ΔH_{LE} for KF, where $\Delta H_{\text{LE}} =$ lattice energy ΔH_{soln} for KF, as for other soluble ionic compounds, is a relatively small number. How can this be since ΔH_{hyd} and ΔH_{LE} are relatively large negative numbers?
- What does the axiom “like dissolves like” mean? There are four types of solute/solvent combinations: polar solutes in polar solvents, nonpolar solutes in polar solvents, and so on. For each type of solution, discuss the magnitude of ΔH_{soln} .
- Structure, pressure, and temperature all have an effect on solubility. Discuss each of their effects. What is Henry’s law? Why does Henry’s law not work for $\text{HCl}(g)$? What do the terms *hydrophobic* and *hydrophilic* mean?

5. Define the terms in Raoult's law. Figure 11.9 illustrates the net transfer of water molecules from pure water to an aqueous solution of a nonvolatile solute. Explain why eventually all of the water from the beaker of pure water will transfer to the aqueous solution. If the experiment illustrated in Fig. 11.9 was performed using a volatile solute, what would happen? How do you calculate the total vapor pressure when both the solute and solvent are volatile?
6. In terms of Raoult's law, distinguish between an ideal liquid–liquid solution and a nonideal liquid–liquid solution. If a solution is ideal, what is true about ΔH_{soln} , ΔT for the solution formation, and the interactive forces within the pure solute and pure solvent as compared to the interactive forces within the solution. Give an example of an ideal solution. Answer the previous two questions for solutions that exhibit either negative or positive deviations from Raoult's law.
7. Vapor-pressure lowering is a colligative property, as are freezing-point depression and boiling-point elevation. What is a colligative property? Why is the freezing point depressed for a solution as compared to the pure solvent? Why is the boiling point elevated for a solution as compared to the pure solvent? Explain how to calculate ΔT for a freezing-point depression problem or a boiling-point elevation problem. Of the solvents listed in Table 11.5, which would have the largest freezing-point depression for a 0.50 molal solution? Which would have the smallest boiling-point elevation for a 0.50 molal solution?
A common application of freezing-point depression and boiling-point elevation experiments is to provide a means to calculate the molar mass of a nonvolatile solute. What data are needed to calculate the molar mass of a nonvolatile solute? Explain how you would manipulate these data to calculate the molar mass of the nonvolatile solute.
8. What is osmotic pressure? How is osmotic pressure calculated? Molarity units are used in the osmotic pressure equation. When does the molarity of a solution approximately equal the molality of the solution? Before refrigeration was common, many foods were preserved by salting them heavily, and many fruits were preserved by mixing them with a large amount of sugar (fruit preserves). How do salt and sugar act as preservatives? Two applications of osmotic pressure are dialysis and desalination. Explain these two processes.
9. Distinguish between a strong electrolyte, a weak electrolyte, and a nonelectrolyte. How can colligative properties be used to distinguish between them? What is the van't Hoff factor? Why is the observed freezing-point depression for electrolyte solutions sometimes less than the calculated value? Is the discrepancy greater for concentrated or dilute solutions?
10. What is a colloidal dispersion? Give some examples of colloids. The Tyndall effect is often used to distinguish between a colloidal suspension and a true solution. Explain. The destruction of a colloid is done through a process called coagulation. What is coagulation?

Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

1. Consider Fig. 11.9. According to the caption and picture, water seems to go from one beaker to another.

- a. Explain why this occurs.
 - b. The explanation in the text uses terms such as *vapor pressure* and *equilibrium*. Explain what these have to do with the phenomenon. For example, what is coming to equilibrium?
 - c. Does all the water end up in the second beaker?
 - d. Is water evaporating from the beaker containing the solution? If so, is the rate of evaporation increasing, decreasing, or staying constant?
- Draw pictures to illustrate your explanations.

2. Once again, consider Fig. 11.9. Suppose instead of having a nonvolatile solute in the solvent in one beaker, the two beakers contain different volatile liquids. That is, suppose one beaker contains liquid A ($P_{\text{vap}} = 50 \text{ torr}$) and the other beaker contains liquid B ($P_{\text{vap}} = 100 \text{ torr}$). Explain what happens as time passes. How is this similar to the first case (shown in the figure)? How is it different?
3. Assume that you place a freshwater plant into a saltwater solution and examine it under a microscope. What happens to the plant cells? What if you placed a saltwater plant in pure water? Explain. Draw pictures to illustrate your explanations.
4. How does ΔH_{soln} relate to deviations from Raoult's law? Explain.
5. You have read that adding a solute to a solvent can both increase the boiling point and decrease the freezing point. A friend of yours explains it to you like this: "The solute and solvent can be like salt in water. The salt gets in the way of freezing in that it blocks the water molecules from joining together. The salt acts like a strong bond holding the water molecules together so that it is harder to boil." What do you say to your friend?
6. You drop an ice cube (made from pure water) into a saltwater solution at 0°C . Explain what happens and why.
7. Using the phase diagram for water and Raoult's law, explain why salt is spread on the roads in winter (even when it is below freezing).
8. You and your friend are each drinking cola from separate 2-L bottles. Both colas are equally carbonated. You are able to drink 1 L of cola, but your friend can drink only about half a liter. You each close the bottles and place them in the refrigerator. The next day when you each go to get the colas, whose will be more carbonated and why?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Solution Review

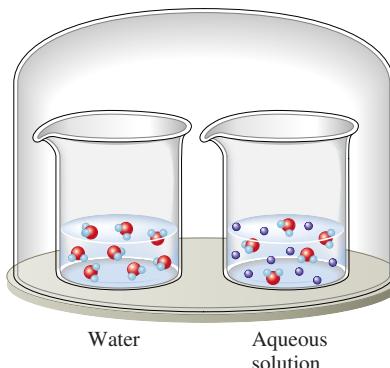
If you have trouble with these exercises, review Sections 4.1 to 4.3 in Chapter 4.

9. Rubbing alcohol contains 585 g of isopropanol ($\text{C}_3\text{H}_7\text{OH}$) per liter (aqueous solution). Calculate the molarity.
10. What volume of a 0.580 M solution of CaCl_2 contains 1.28 g of solute?
11. Calculate the sodium ion concentration when 70.0 mL of 3.0 M sodium carbonate is added to 30.0 mL of 1.0 M sodium bicarbonate.
12. Write equations showing the ions present after the following strong electrolytes are dissolved in water.
- | | | |
|-------------------------------|---------------------------|-----------------------------|
| a. HNO_3 | d. SrBr_2 | g. NH_4NO_3 |
| b. Na_2SO_4 | e. KClO_4 | h. CuSO_4 |
| c. $\text{Al}(\text{NO}_3)_3$ | f. NH_4Br | i. NaOH |

Questions

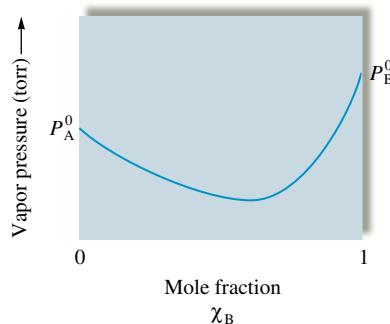
13. Rationalize the temperature dependence of the solubility of a gas in water in terms of the kinetic molecular theory.
14. The weak electrolyte $\text{NH}_3(g)$ does not obey Henry's law. Why? $\text{O}_2(g)$ obeys Henry's law in water but not in blood (an aqueous solution). Why?

15. The two beakers in the sealed container illustrated below contain pure water and an aqueous solution of a volatile solute.



If the solute is less volatile than water, explain what will happen to the volumes in the two containers as time passes.

16. The following plot shows the vapor pressure of various solutions of components A and B at some temperature.



Which of the following statements is false concerning solutions of A and B?

- The solutions exhibit negative deviations from Raoult's law.
 - ΔH_{mix} for the solutions should be exothermic.
 - The intermolecular forces are stronger in solution than in either pure A or pure B.
 - Pure liquid B is more volatile than pure liquid A.
 - The solution with $\chi_B = 0.6$ will have a lower boiling point than either pure A or pure B.
17. When pure methanol is mixed with water, the resulting solution feels warm. Would you expect this solution to be ideal? Explain.
18. Detergent molecules can stabilize the emulsion of oil in water as well as remove dirt from soiled clothes. A typical detergent is sodium dodecylsulfate, or SDS, and it has a formula of $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{SO}_4^-\text{Na}^+$. In aqueous solution, SDS suspends oil or dirt by forming small aggregates of detergent anions called *micelles*. Propose a structure for micelles.
19. For an acid or a base, when is the normality of a solution equal to the molarity of the solution and when are the two concentration units different?
20. In order for sodium chloride to dissolve in water, a small amount of energy must be added during solution formation. This is not energetically favorable. Why is NaCl so soluble in water?

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- 21.** Which of the following statements is(are) true? Correct the false statements.
- The vapor pressure of a solution is directly related to the mole fraction of solute.
 - When a solute is added to water, the water in solution has a lower vapor pressure than that of pure ice at 0°C.
 - Colligative properties depend only on the identity of the solute and not on the number of solute particles present.
 - When sugar is added to water, the boiling point of the solution increases above 100°C because sugar has a higher boiling point than water.
- 22.** Is the following statement true or false? Explain your answer. When determining the molar mass of a solute using boiling point of freezing point data, camphor would be the best solvent choice of all of the solvents listed in Table 11.5.
- 23.** Explain the terms isotonic solution, crenation, and hemolysis.
- 24.** What is ion pairing?

Exercises

In this section similar exercises are paired.

Concentration of Solutions

- 25.** A solution of phosphoric acid was made by dissolving 10.0 g of H_3PO_4 in 100.0 mL of water. The resulting volume was 104 mL. Calculate the density, mole fraction, molarity, and molality of the solution. Assume water has a density of 1.00 g/cm^3 .
- 26.** An aqueous antifreeze solution is 40.0% ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) by mass. The density of the solution is 1.05 g/cm^3 . Calculate the molality, molarity, and mole fraction of the ethylene glycol.
- 27.** Common commercial acids and bases are aqueous solutions with the following properties:

	Density (g/cm^3)	Mass Percent of Solute
Hydrochloric acid	1.19	38
Nitric acid	1.42	70.
Sulfuric acid	1.84	95
Acetic acid	1.05	99
Ammonia	0.90	28

Calculate the molarity, molality, and mole fraction of each of the preceding reagents.

- 28.** In lab you need to prepare at least 100 mL of each of the following solutions. Explain how you would proceed using the given information.
- 2.0 *m* KCl in water (density of H_2O = 1.00 g/cm^3)
 - 15% NaOH by mass in water ($d = 1.00 \text{ g}/\text{cm}^3$)
 - 25% NaOH by mass in CH_3OH ($d = 0.79 \text{ g}/\text{cm}^3$)
 - 0.10 mole fraction of $\text{C}_6\text{H}_{12}\text{O}_6$ in water ($d = 1.00 \text{ g}/\text{cm}^3$)
- 29.** A solution is prepared by mixing 25 mL pentane (C_5H_{12} , $d = 0.63 \text{ g}/\text{cm}^3$) with 45 mL hexane (C_6H_{14} , $d = 0.66 \text{ g}/\text{cm}^3$). Assuming that the volumes add on mixing, calculate the mass percent, mole fraction, molality, and molarity of the pentane.

- 30.** A bottle of wine contains 12.5% ethanol by volume. The density of ethanol ($\text{C}_2\text{H}_5\text{OH}$) is 0.789 g/cm^3 . Calculate the concentration of ethanol in wine in terms of mass percent and molality.

- 31.** A 1.37 *M* solution of citric acid ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$) in water has a density of 1.10 g/cm^3 . Calculate the mass percent, molality, mole fraction, and normality of the citric acid. Citric acid has three acidic protons.
- 32.** Calculate the molarity and mole fraction of acetone in a 1.00 *m* solution of acetone (CH_3COCH_3) in ethanol ($\text{C}_2\text{H}_5\text{OH}$). (Density of acetone = 0.788 g/cm^3 ; density of ethanol = 0.789 g/cm^3 .) Assume that the volumes of acetone and ethanol add.

Energetics of Solutions and Solubility

- 33.** The lattice energy* of NaI is -686 kJ/mol , and the enthalpy of hydration is -694 kJ/mol . Calculate the enthalpy of solution per mole of solid NaI . Describe the process to which this enthalpy change applies.
- 34.** a. Use the following data to calculate the enthalpy of hydration for calcium chloride and calcium iodide.

	Lattice Energy	ΔH_{soln}
$\text{CaCl}_2(s)$	-2247 kJ/mol	-46 kJ/mol
$\text{CaI}_2(s)$	-2059 kJ/mol	-104 kJ/mol

- b. Based on your answers to part a, which ion, Cl^- or I^- , is more strongly attracted to water?
- 35.** Although $\text{Al}(\text{OH})_3$ is insoluble in water, NaOH is very soluble. Explain in terms of lattice energies.
- 36.** The high melting points of ionic solids indicate that a lot of energy must be supplied to separate the ions from one another. How is it possible that the ions can separate from one another when soluble ionic compounds are dissolved in water, often with essentially no temperature change?
- 37.** Which solvent, water or carbon tetrachloride, would you choose to dissolve each of the following?
- KrF_2
 - SF_2
 - SO_2
 - CO_2
 - MgF_2
 - CH_2O
 - $\text{CH}_2=\text{CH}_2$
- 38.** Which solvent, water or hexane (C_6H_{14}), would you choose to dissolve each of the following?
- NaCl
 - HF
 - $\text{octane} (\text{C}_8\text{H}_{18})$
 - $(\text{NH}_4)_2\text{SO}_4$
- 39.** What factors cause one solute to be more strongly attracted to water than another? For each of the following pairs, predict which substance would be more soluble in water.
- $\text{CH}_3\text{CH}_2\text{OH}$ or $\text{CH}_3\text{CH}_2\text{CH}_3$
 - CHCl_3 or CCl_4
 - $\text{CH}_3\text{CH}_2\text{OH}$ or $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{OH}$

*Lattice energy was defined in Chapter 8 as the energy change for the process $\text{M}^+(g) + \text{X}^-(g) \rightarrow \text{MX}(s)$.

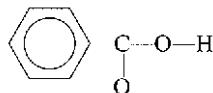
40. Which ion in each of the following pairs would you expect to be more strongly hydrated? Why?

- a. Na^+ or Mg^{2+} d. F^- or Br^-
 b. Mg^{2+} or Be^{2+} e. Cl^- or ClO_4^-
 c. Fe^{2+} or Fe^{3+} f. ClO_4^- or SO_4^{2-}

41. Rationalize the trend in water solubility for the following simple alcohols:

Alcohol	Solubility (g/100 g H_2O at 20°C)
Methanol, CH_3OH	Soluble in all proportions
Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$	Soluble in all proportions
Propanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	Soluble in all proportions
Butanol, $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$	8.14
Pentanol, $\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$	2.64
Hexanol, $\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OH}$	0.59
Heptanol, $\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{OH}$	0.09

42. The solubility of benzoic acid ($\text{HC}_7\text{H}_5\text{O}_2$),



is 0.34 g/100 mL in water at 25°C and is 10.0 g/100 mL in benzene (C_6H_6) at 25°C. Rationalize this solubility behavior. (Hint: Benzoic acid forms a dimer in benzene.) Would benzoic acid be more or less soluble in a 0.1 M NaOH solution than it is in water? Explain.

43. The solubility of nitrogen in water is 8.21×10^{-4} mol/L at 0°C when the N_2 pressure above water is 0.790 atm. Calculate the Henry's law constant for N_2 in units of mol/L · atm for Henry's law in the form $C = kP$, where C is the gas concentration in mol/L. Calculate the solubility of N_2 in water when the partial pressure of nitrogen above water is 1.10 atm at 0°C.

44. In Exercise 107 in Chapter 5, the pressure of CO_2 in a bottle of sparkling wine was calculated assuming that the CO_2 was insoluble in water. This was a bad assumption. Redo this problem by assuming that CO_2 obeys Henry's law. Use the data given in that problem to calculate the partial pressure of CO_2 in the gas phase and the solubility of CO_2 in the wine at 25°C. The Henry's law constant for CO_2 is 3.1×10^{-2} mol/L · atm at 25°C with Henry's law in the form $C = kP$, where C is the concentration of the gas in mol/L.

Vapor Pressures of Solutions

45. Glycerin, $\text{C}_3\text{H}_8\text{O}_3$, is a nonvolatile liquid. What is the vapor pressure of a solution made by adding 164 g of glycerin to 338 mL of H_2O at 39.8°C? The vapor pressure of pure water at 39.8°C is 54.74 torr and its density is 0.992 g/cm³.

46. The vapor pressure of a solution containing 53.6 g glycerin ($\text{C}_3\text{H}_8\text{O}_3$) in 133.7 g ethanol ($\text{C}_2\text{H}_5\text{OH}$) is 113 torr at 40°C. Calculate the vapor pressure of pure ethanol at 40°C assuming that glycerin is a nonvolatile, nonelectrolyte solute in ethanol.

47. At a certain temperature, the vapor pressure of pure benzene (C_6H_6) is 0.930 atm. A solution was prepared by dissolving 10.0 g of a nondissociating, nonvolatile solute in 78.11 g of benzene at that temperature. The vapor pressure of the solution was found to be 0.900 atm. Assuming the solution behaves ideally, determine the molar mass of the solute.

48. A solution of sodium chloride in water has a vapor pressure of 19.6 torr at 25°C. What is the mole fraction of NaCl solute particles in this solution? What would be the vapor pressure of this solution at 45°C? The vapor pressure of pure water is 23.8 torr at 25°C and 71.9 torr at 45°C and assume sodium chloride exists as Na^+ and Cl^- ions in solution.

49. Pentane (C_5H_{12}) and hexane (C_6H_{14}) form an ideal solution. At 25°C the vapor pressures of pentane and hexane are 511 and 150. torr, respectively. A solution is prepared by mixing 25 mL pentane (density, 0.63 g/mL) with 45 mL hexane (density, 0.66 g/mL).
- What is the vapor pressure of the resulting solution?
 - What is the composition by mole fraction of pentane in the vapor that is in equilibrium with this solution?

50. A solution is prepared by mixing 0.0300 mol CH_2Cl_2 and 0.0500 mol CH_2Br_2 at 25°C. Assuming the solution is ideal, calculate the composition of the vapor (in terms of mole fractions) at 25°C. At 25°C, the vapor pressures of pure CH_2Cl_2 and pure CH_2Br_2 are 133 and 11.4 torr, respectively.

51. What is the composition of a methanol (CH_3OH)–propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) solution that has a vapor pressure of 174 torr at 40°C? At 40°C, the vapor pressures of pure methanol and pure propanol are 303 and 44.6 torr, respectively. Assume the solution is ideal.

52. Benzene and toluene form an ideal solution. Consider a solution of benzene and toluene prepared at 25°C. Assuming the mole fractions of benzene and toluene in the vapor phase are equal, calculate the composition of the solution. At 25°C the vapor pressures of benzene and toluene are 95 and 28 torr, respectively.

53. Which of the following will have the lowest total vapor pressure at 25°C?

- pure water (vapor pressure = 23.8 torr at 25°C)
- a solution of glucose in water with $\chi_{\text{C}_6\text{H}_{12}\text{O}_6} = 0.01$
- a solution of sodium chloride in water with $\chi_{\text{NaCl}} = 0.01$
- a solution of methanol in water with $\chi_{\text{CH}_3\text{OH}} = 0.2$ (Consider the vapor pressure of both methanol [143 torr at 25°C] and water.)

54. Which of the choices in Exercise 53 has the highest vapor pressure?

55. A solution is made by mixing 50.0 g acetone (CH_3COCH_3) and 50.0 g methanol (CH_3OH). What is the vapor pressure of this solution at 25°C? What is the composition of the vapor expressed as a mole fraction? Assume ideal solution and gas behavior. (At 25°C the vapor pressures of pure acetone and pure methanol are 271 and 143 torr, respectively.) The actual vapor pressure of this solution is 161 torr. Explain any discrepancies.

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56. The vapor pressures of several solutions of water–propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) were determined at various compositions, with the following data collected at 45°C:

$\chi_{\text{H}_2\text{O}}$	Vapor pressure (torr)
0	74.0
0.15	77.3
0.37	80.2
0.54	81.6
0.69	80.6
0.83	78.2
1.00	71.9

- a. Are solutions of water and propanol ideal? Explain.
- b. Predict the sign of ΔH_{soln} for water–propanol solutions.
- c. Are the interactive forces between propanol and water molecules weaker than, stronger than, or equal to the interactive forces between the pure substances? Explain.
- d. Which of the solutions in the data would have the lowest normal boiling point?

Colligative Properties

57. A solution is prepared by dissolving 27.0 g of urea, $(\text{NH}_2)_2\text{CO}$, in 150.0 g of water. Calculate the boiling point of the solution. Urea is a nonelectrolyte.
58. A 2.00-g sample of a large biomolecule was dissolved in 15.0 g of carbon tetrachloride. The boiling point of this solution was determined to be 77.85°C. Calculate the molar mass of the biomolecule. For carbon tetrachloride, the boiling-point constant is $5.03^\circ\text{C} \cdot \text{kg/mol}$, and the boiling point of pure carbon tetrachloride is 76.50°C.
59. What mass of glycerin ($\text{C}_3\text{H}_8\text{O}_3$), a nonelectrolyte, must be dissolved in 200.0 g water to give a solution with a freezing point of -1.50°C ?
60. The freezing point of *t*-butanol is 25.50°C and K_f is $9.1^\circ\text{C} \cdot \text{kg/mol}$. Usually *t*-butanol absorbs water on exposure to air. If the freezing point of a 10.0-g sample of *t*-butanol is 24.59°C , how many grams of water are present in the sample?
61. Calculate the freezing point and boiling point of an antifreeze solution that is 50.0% by mass of ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) in water. Ethylene glycol is a nonelectrolyte.
62. What volume of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), a nonelectrolyte, must be added to 15.0 L of water to produce an antifreeze solution with a freezing point of -25.0°C ? What is the boiling point of this solution? (The density of ethylene glycol is 1.11 g/cm^3 , and the density of water is 1.00 g/cm^3 .)
63. Thyroxine, an important hormone that controls the rate of metabolism in the body, can be isolated from the thyroid gland. When 0.455 g of thyroxine is dissolved in 10.0 g of benzene, the freezing point of the solution is depressed by 0.300°C . What is the molar mass of thyroxine? See Table 11.5.
64. Anthraquinone contains only carbon, hydrogen, and oxygen and has an empirical formula of $\text{C}_7\text{H}_4\text{O}$. The freezing point of camphor is lowered by 22.3°C when 1.32 g anthraquinone is dissolved in 11.4 g camphor. Determine the molecular formula of anthraquinone.

65. a. Calculate the freezing-point depression and osmotic pressure at 25°C of an aqueous solution containing 1.0 g/L of a protein (molar mass = $9.0 \times 10^4 \text{ g/mol}$) if the density of the solution is 1.0 g/cm^3 .

- b. Considering your answer to part a, which colligative property, freezing-point depression or osmotic pressure, would be better used to determine the molar masses of large molecules? Explain.

66. An aqueous solution of 10.00 g of catalase, an enzyme found in the liver, has a volume of 1.00 L at 27°C . The solution's osmotic pressure at 27°C is found to be 0.74 torr. Calculate the molar mass of catalase.

67. If the human eye has an osmotic pressure of 8.00 atm at 25°C , what concentration of solute particles in water will provide an isotonic eyeglass solution (a solution with equal osmotic pressure)?

68. How would you prepare 1.0 L of an aqueous solution of sodium chloride having an osmotic pressure of 15 atm at 22°C ? Assume sodium chloride exists as Na^+ and Cl^- ions in solution.

Properties of Electrolyte Solutions

69. Consider the following solutions:

0.010 *m* Na_3PO_4 in water

0.020 *m* CaBr_2 in water

0.020 *m* KCl in water

0.020 *m* HF in water (HF is a weak acid.)

- a. Assuming complete dissociation of the soluble salts, which solution(s) would have the same boiling point as 0.040 *m* $\text{C}_6\text{H}_{12}\text{O}_6$ in water? $\text{C}_6\text{H}_{12}\text{O}_6$ is a nonelectrolyte.

- b. Which solution would have the highest vapor pressure at 28°C ?
c. Which solution would have the largest freezing-point depression?

70. From the following:

pure water

solution of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (*m* = 0.01) in water

solution of NaCl (*m* = 0.01) in water

solution of CaCl_2 (*m* = 0.01) in water

choose the one with the

- a. highest freezing point.
- b. lowest freezing point.
- c. highest boiling point.
- d. lowest boiling point.
- e. highest osmotic pressure.

71. Calculate the freezing point and the boiling point of each of the following aqueous solutions. (Assume complete dissociation.)

a. 0.050 *m* MgCl_2

b. 0.050 *m* FeCl_3

72. A water desalination plant is set up near a salt marsh containing water that is 0.10 *M* NaCl . Calculate the minimum pressure that must be applied at 20°C to purify the water by reverse osmosis. Assume NaCl is completely dissociated.

73. Use the following data for three aqueous solutions of CaCl_2 to calculate the apparent value of the van't Hoff factor.

Molality	Freezing-Point Depression ($^\circ\text{C}$)
0.0225	0.110
0.0910	0.440
0.278	1.330

- 74.** Calculate the freezing point and the boiling point of each of the following solutions using the observed van't Hoff factors in Table 11.6.

a. 0.050 M MgCl_2 b. 0.050 M FeCl_3

- 75.** In the winter of 1994, record low temperatures were registered throughout the United States. For example, in Champaign, Illinois, a record low of -29°F was registered. At this temperature can salting icy roads with CaCl_2 be effective in melting the ice?
- Assume $i = 3.00$ for CaCl_2 .
 - Assume the average value of i from Exercise 73.
- (The solubility of CaCl_2 in cold water is 74.5 g per 100.0 g of water.)

- 76.** A 0.500-g sample of a compound is dissolved in enough water to form 100.0 mL of solution. This solution has an osmotic pressure of 2.50 atm at 25°C . If each molecule of the solute dissociates into two particles (in this solvent), what is the molar mass of this solute?

Additional Exercises

- 77.** In a coffee-cup calorimeter, 1.60 g of NH_4NO_3 was mixed with 75.0 g of water at an initial temperature of 25.00°C . After dissolution of the salt, the final temperature of the calorimeter contents was 23.34°C .

- Assuming the solution has a heat capacity of $4.18\text{ J/g} \cdot {}^\circ\text{C}$, and assuming no heat loss to the calorimeter, calculate the enthalpy of solution (ΔH_{soln}) for the dissolution of NH_4NO_3 in units of kJ/mol.
- If the enthalpy of hydration for NH_4NO_3 is -630. kJ/mol , calculate the lattice energy of NH_4NO_3 .

- 78.** In flushing and cleaning columns used in liquid chromatography to remove adsorbed contaminants, a series of solvents is used. Hexane (C_6H_{14}), chloroform (CHCl_3), methanol (CH_3OH), and water are passed through the column in that order. Rationalize the order in terms of intermolecular forces and the mutual solubility (miscibility) of the solvents.

- 79.** Explain the following on the basis of the behavior of atoms and/or ions.
- Cooking with water is faster in a pressure cooker than in an open pan.
 - Salt is used on icy roads.
 - Melted sea ice from the Arctic Ocean produces fresh water.
 - $\text{CO}_2(s)$ (dry ice) does not have a normal boiling point under normal atmospheric conditions, even though CO_2 is a liquid in fire extinguishers.
 - Adding a solute to a solvent extends the liquid phase over a larger temperature range.

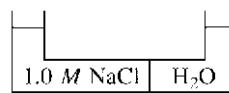
- 80.** The term "proof" is defined as twice the percent by volume of pure ethanol in solution. Thus, a solution that is 95% (by volume) ethanol is 190 proof. What is the molarity of ethanol in a 92 proof ethanol/water solution? Assume the density of ethanol, $\text{C}_2\text{H}_5\text{OH}$, is 0.79 g/cm^3 and the density of water is 1.0 g/cm^3 .

- 81.** At 25°C , the vapor in equilibrium with a solution containing carbon disulfide and acetonitrile has a total pressure of 263 torr and is 85.5 mole percent carbon disulfide. What is the mole fraction of carbon disulfide in the solution? At 25°C , the vapor pressure of carbon disulfide is 375 torr. Assume the solution and vapor exhibit ideal behavior.

- 82.** If the fluid inside a tree is about 0.1 M more concentrated in solute than the groundwater that bathes the roots, how high will a column of fluid rise in the tree at 25°C ? Assume that the density of the fluid is 1.0 g/cm^3 . (The density of mercury is 13.6 g/cm^3 .)

- 83.** An unknown compound contains only carbon, hydrogen, and oxygen. Combustion analysis of the compound gives mass percents of 31.57% C and 5.30% H. The molar mass is determined by measuring the freezing-point depression of an aqueous solution. A freezing point of -5.20°C is recorded for a solution made by dissolving 10.56 g of the compound in 25.0 g water. Determine the empirical formula, molar mass, and molecular formula of the compound. Assume that the compound is a nonelectrolyte.

- 84.** Consider the following:



What would happen to the level of liquid in the two arms if the semipermeable membrane separating the two liquids were permeable to

- H_2O only?
- H_2O , Na^+ , and Cl^- ?

- 85.** Consider an aqueous solution containing sodium chloride that has a density of 1.01 g/mL . Assume the solution behaves ideally. The freezing point of this solution at 1.0 atm is -1.28°C . Calculate the percent composition of this solution (by mass).

- 86.** What stabilizes a colloidal suspension? Explain why adding heat or adding an electrolyte can cause the suspended particles to settle out.

- 87.** The freezing point of an aqueous solution is -2.79°C .

- Determine the boiling point of this solution.
- Determine the vapor pressure (in mm Hg) of this solution at 25°C (the vapor pressure of pure water at 25°C is 23.76 mm Hg).
- Explain any assumptions you make in solving parts a and b.

Challenge Problems

- 88.** The vapor pressure of pure benzene is 750.0 torr and the vapor pressure of toluene is 300.0 torr at a certain temperature. You make a solution by pouring "some" benzene with "some" toluene. You then place this solution in a closed container and wait for the vapor to come into equilibrium with the solution. Next, you condense the vapor. You put this liquid (the condensed vapor) in a closed container and wait for the vapor to come into equilibrium with the solution. You then condense this vapor and find the mole fraction of benzene in this vapor to be 0.714. Determine the mole fraction of benzene in the original solution assuming the solution behaves ideally.

- 89.** Liquid A has vapor pressure x , and liquid B has vapor pressure y . What is the mole fraction of the liquid mixture if the vapor above the solution is 30% A by moles? 50% A? 80% A? (Calculate in terms of x and y .)

Liquid A has vapor pressure x , liquid B has vapor pressure y . What is the mole fraction of the vapor above the solution if the liquid mixture is 30% A by moles? 50% A? 80% A? (Calculate in terms of x and y .)

524 Chapter Eleven Properties of Solutions

- 90.** Erythrocytes are red blood cells containing hemoglobin. In a saline solution they shrivel when the salt concentration is high and swell when the salt concentration is low. In a 25°C aqueous solution of NaCl, whose freezing point is -0.406°C , erythrocytes neither swell nor shrink. If we want to calculate the osmotic pressure of the solution inside the erythrocytes under these conditions, what do we need to assume? Why? Estimate how good (or poor) of an assumption this is. Make this assumption and calculate the osmotic pressure of the solution inside the erythrocytes.
- 91.** You make 20.0 g of a sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) and NaCl mixture and dissolve it in 1.00 kg of water. The freezing point of this solution is found to be -0.426°C . Assuming ideal behavior, calculate the mass percent composition of the original mixture, and the mole fraction of sucrose in the original mixture.
- 92.** An aqueous solution is 1.00% NaCl by mass and has a density of 1.071 g/cm³ at 25°C. The observed osmotic pressure of this solution is 7.83 atm at 25°C.
- What fraction of the moles of NaCl in this solution exist as ion pairs?
 - Calculate the freezing point that would be observed for this solution.
- 93.** The vapor in equilibrium with a pentane–hexane solution at 25°C has a mole fraction of pentane equal to 0.15 at 25°C. What is the mole fraction of pentane in the solution? (See Exercise 49 for the vapor pressures of the pure liquids.)
- 94.** A forensic chemist is given a white solid that is suspected of being pure cocaine ($\text{C}_{17}\text{H}_{21}\text{NO}_4$, molar mass = 303.35 g/mol). She dissolves 1.22 ± 0.01 g of the solid in 15.60 ± 0.01 g benzene. The freezing point is lowered by $1.32 \pm 0.04^{\circ}\text{C}$.
- What is the molar mass of the substance? Assuming that the percent uncertainty in the calculated molar mass is the same as the percent uncertainty in the temperature change, calculate the uncertainty in the molar mass.
 - Could the chemist unequivocally state that the substance is cocaine? For example, is the uncertainty small enough to distinguish cocaine from codeine ($\text{C}_{18}\text{H}_{21}\text{NO}_3$, molar mass = 299.36 g/mol)?
 - Assuming that the absolute uncertainties in the measurements of temperature and mass remain unchanged, how could the chemist improve the precision of her results?
- 95.** A 1.60-g sample of a mixture of naphthalene (C_{10}H_8) and anthracene ($\text{C}_{14}\text{H}_{10}$) is dissolved in 20.0 g benzene (C_6H_6). The freezing point of the solution is 2.81°C . What is the composition as mass percent of the sample mixture? The freezing point of benzene is 5.51°C , and K_f is $5.12^{\circ}\text{C} \cdot \text{kg/mol}$.
- 96.** A solid mixture contains MgCl₂ and NaCl. When 0.5000 g of this solid is dissolved in enough water to form 1.000 L of solution, the osmotic pressure at 25.0°C is observed to be 0.3950 atm. What is the mass percent of MgCl₂ in the solid? (Assume ideal behavior for the solution.)
- 97.** Formic acid (HCO₂H) is a monoprotic acid that ionizes only partially in aqueous solutions. A 0.10 M formic acid solution is 4.2% ionized. Assuming that the molarity and molality of the solution are the same, calculate the freezing point and the boiling point of 0.10 M formic acid.
- 98.** Specifications for lactated Ringer's solution, which is used for intravenous (IV) injections, are as follows to reach 100. mL of solution:
- 285–315 mg Na⁺
14.1–17.3 mg K⁺
4.9–6.0 mg Ca²⁺
368–408 mg Cl⁻
231–261 mg lactate, C₃H₅O₃⁻
- Specify the amounts of NaCl, KCl, CaCl₂ · 2H₂O, and NaC₃H₅O₃ needed to prepare 100. mL of lactated Ringer's solution.
 - What is the range of the osmotic pressure of the solution at 37°C, given the above specifications?
- 99.** In some regions of the southwest United States, the water is very hard. For example, in Las Cruces, New Mexico, the tap water contains about 560 µg of dissolved solids per milliliter. Reverse osmosis units are marketed in this area to soften water. A typical unit exerts a pressure of 8.0 atm and can produce 45 L of water per day.
- Assuming all of the dissolved solids are MgCO₃ and assuming a temperature of 27°C, what total volume of water must be processed to produce 45 L of pure water?
 - Would the same system work for purifying seawater? (Assume seawater is 0.60 M NaCl.)

Integrative Problems

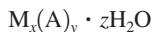
These problems require the integration of multiple concepts to find the solutions.

- 100.** Creatinine, C₄H₇N₃O, is a by-product of muscle metabolism, and creatinine levels in the body are known to be a fairly reliable indicator of kidney function. The normal level of creatinine in the blood for adults is approximately 1.0 mg per deciliter (dL) of blood. If the density of blood is 1.025 g/mL, calculate the molality of a normal creatinine level in a 10.0-mL blood sample. What is the osmotic pressure of this solution at 25.0°C?
- 101.** An aqueous solution containing 0.250 mol of Q, a strong electrolyte, in 5.00×10^2 g of water freezes at -2.79°C . What is the van't Hoff factor for Q? The molal freezing-point depression constant for water is $1.86^{\circ}\text{C} \cdot \text{kg/mol}$. What is the formula of Q if it is 38.68% chlorine by mass and there are twice as many anions as cations in one formula unit of Q?
- 102.** Patients undergoing an upper gastrointestinal tract laboratory test are typically given an X-ray contrast agent that aids with the radiologic imaging of the anatomy. One such contrast agent is sodium diatrizoate, a nonvolatile water-soluble compound. A 0.378 m solution is prepared by dissolving 38.4 g of sodium diatrizoate (NaDTZ) in 1.60×10^2 mL of water at 31.2°C (the density of water at 31.2°C is 0.995 g/mL). What is the molar mass of sodium diatrizoate? What is the vapor pressure of this solution if the vapor pressure of pure water at 31.2°C is 34.1 torr?

Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

- 103.** Using the following information, identify the strong electrolyte whose general formula is



Ignore the effect of interionic attractions in the solution.

- a. Aⁿ⁻ is a common oxyanion. When 30.0 mg of the anhydrous sodium salt containing this oxyanion (Na_nA, where n = 1, 2, or 3) is reduced, 15.26 mL of 0.02313 M reducing agent is required to react completely with the Na_nA present. Assume a 1:1 mole ratio in the reaction.

- b. The cation is derived from a silvery white metal that is relatively expensive. The metal itself crystallizes in a body-centered cubic unit cell and has an atomic radius of 198.4 pm. The solid, pure metal has a density of 5.243 g/cm³. The oxidation number of M in the strong electrolyte in question is +3.
- c. When 33.45 mg of the compound is present (dissolved) in 10.0 mL of aqueous solution at 25°C, the solution has an osmotic pressure of 558 torr.



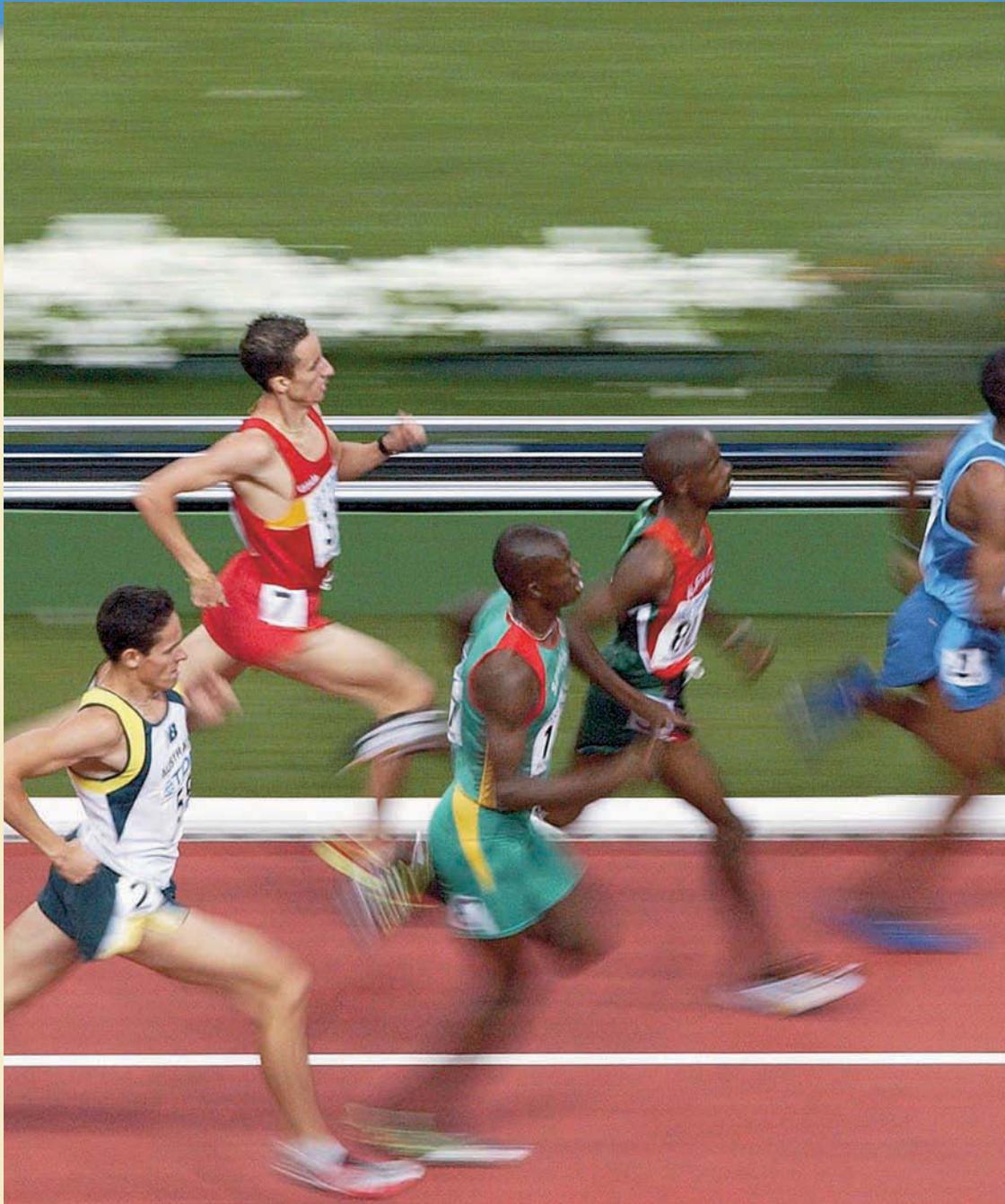
Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmc.com/PIC/zumdahl7e.

*This Marathon Problem was developed by James H. Burness, Penn State University, York Campus. Reprinted with permission from the *Journal of Chemical Education*, Vol. 68, No. 11, 1991, pp. 919–922; copyright © 1991, Division of Chemical Education, Inc.

12 Chemical Kinetics

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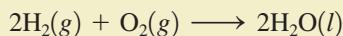
The kinetic energy of these world championship runners is evident in the 800-meter race at Saint-Denis, France.



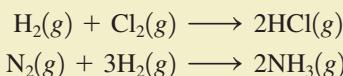
Visualization: Coffee Creamer Flammability

T

The applications of chemistry focus largely on chemical reactions, and the commercial use of a reaction requires knowledge of several of its characteristics, including its stoichiometry, energetics, and rate. A reaction is defined by its reactants and products, whose identity must be learned by experiment. Once the reactants and products are known, the equation for the reaction can be written and balanced, and stoichiometric calculations can be carried out. Another very important characteristic of a reaction is its spontaneity. Spontaneity refers to the *inherent tendency* for the process to occur; however, it implies nothing about speed. *Spontaneous does not mean fast.* There are many spontaneous reactions that are so slow that no apparent reaction occurs over a period of weeks or years at normal temperatures. For example, there is a strong inherent tendency for gaseous hydrogen and oxygen to combine, that is,



but in fact the two gases can coexist indefinitely at 25°C. Similarly, the gaseous reactions



are both highly likely to occur from a thermodynamic standpoint, but we observe no reactions under normal conditions. In addition, the process of changing diamond to graphite is spontaneous but is so slow that it is not detectable.

To be useful, reactions must occur at a reasonable rate. To produce the 20 million tons of ammonia needed each year for fertilizer, we cannot simply mix nitrogen and hydrogen gases at 25°C and wait for them to react. It is not enough to understand the stoichiometry and thermodynamics of a reaction; we also must understand the factors that govern the rate of the reaction. The area of chemistry that concerns reaction rates is called **chemical kinetics**.

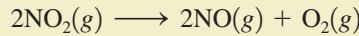
One of the main goals of chemical kinetics is to understand the steps by which a reaction takes place. This series of steps is called the *reaction mechanism*. Understanding the mechanism allows us to find ways to facilitate the reaction. For example, the Haber process for the production of ammonia requires high temperatures to achieve commercially feasible reaction rates. However, even higher temperatures (and more cost) would be required without the use of iron oxide, which speeds up the reaction.

In this chapter we will consider the main ideas of chemical kinetics. We will explore rate laws, reaction mechanisms, and simple models for chemical reactions.

12.1 Reaction Rates

The kinetics of air pollution is discussed in Section 12.8.

To introduce the concept of the rate of a reaction, we will consider the decomposition of nitrogen dioxide, a gas that causes air pollution. Nitrogen dioxide decomposes to nitric oxide and oxygen as follows:



Suppose in a particular experiment we start with a flask of nitrogen dioxide at 300°C and measure the concentrations of nitrogen dioxide, nitric oxide, and oxygen as the nitrogen dioxide decomposes. The results of this experiment are summarized in Table 12.1, and the data are plotted in Fig. 12.1.



The energy required for athletic exertion, the breaching of an Orca whale, and the combustion of fuel in a race car all result from chemical reactions.

Note from these results that the concentration of the reactant (NO_2) decreases with time and the concentrations of the products (NO and O₂) increase with time (see Fig. 12.2). Chemical kinetics deals with the speed at which these changes occur. The speed, or *rate*, of a process is defined as the change in a given quantity over a specific period of time. For chemical reactions, the quantity that changes is the amount or concentration of a reactant or product. So the **reaction rate** of a chemical reaction is defined as the *change in concentration of a reactant or product per unit time*:

$$\begin{aligned} \text{Rate} &= \frac{\text{concentration of A at time } t_2 - \text{concentration of A at time } t_1}{t_2 - t_1} \\ &= \frac{\Delta[\text{A}]}{\Delta t} \end{aligned}$$

[A] means concentration of A in mol/L.

TABLE 12.1 Concentrations of Reactant and Products as a Function of Time for the Reaction $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$ (at 300°C)

Time (± 1 s)	Concentration (mol/L)		
	NO_2	NO	O_2
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

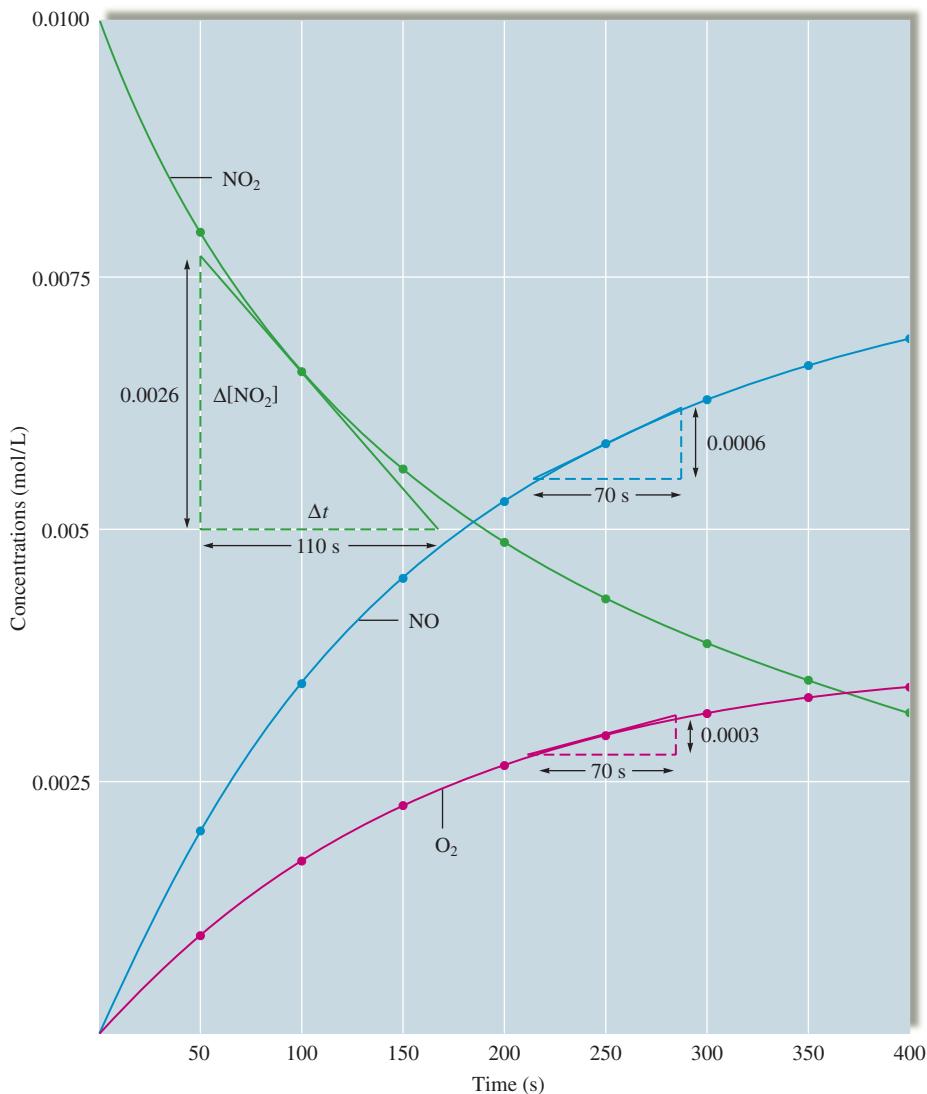


FIGURE 12.1

Starting with a flask of nitrogen dioxide at 300°C, the concentrations of nitrogen dioxide, nitric oxide, and oxygen are plotted versus time.

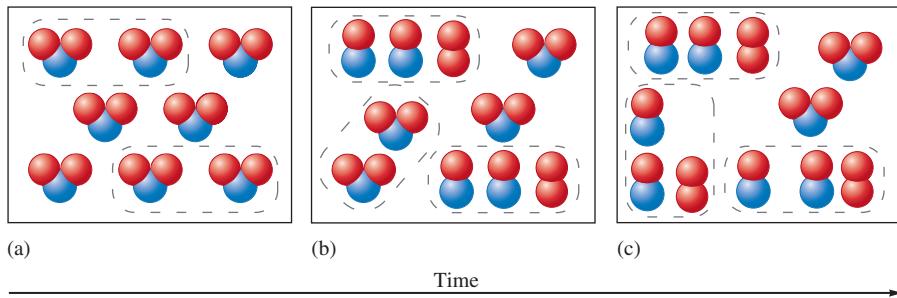


FIGURE 12.2

Representation of the reaction $2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g)$. (a) The reaction at the very beginning ($t = 0$). (b) and (c) As time passes, NO_2 is converted to NO and O_2 .

where A is the reactant or product being considered, and the square brackets indicate concentration in mol/L. As usual, the symbol Δ indicates a *change* in a given quantity. Note that a change can be positive (increase) or negative (decrease), thus leading to a positive or negative reaction rate by this definition. However, for convenience, we will always define the rate as a positive quantity, as we will see.

Now let us calculate the average rate at which the concentration of NO_2 changes over the first 50 seconds of the reaction using the data given in Table 12.1.

$$\begin{aligned}\frac{\text{Change in } [\text{NO}_2]}{\text{Time elapsed}} &= \frac{\Delta[\text{NO}_2]}{\Delta t} \\ &= \frac{[\text{NO}_2]_{t=50} - [\text{NO}_2]_{t=0}}{50. \text{ s} - 0 \text{ s}} \\ &= \frac{0.0079 \text{ mol/L} - 0.0100 \text{ mol/L}}{50. \text{ s}} \\ &= -4.2 \times 10^{-5} \text{ mol/L} \cdot \text{s}\end{aligned}$$

Note that since the concentration of NO_2 decreases with time, $\Delta[\text{NO}_2]$ is a negative quantity. Because it is customary to work with *positive* reaction rates, we define the rate of this particular reaction as

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t}$$

Since the concentrations of reactants always decrease with time, any rate expression involving a reactant will include a negative sign. The average rate of this reaction from 0 to 50 seconds is then

$$\begin{aligned}\text{Rate} &= -\frac{\Delta[\text{NO}_2]}{\Delta t} \\ &= -(4.2 \times 10^{-5} \text{ mol/L} \cdot \text{s}) \\ &\equiv 4.2 \times 10^{-5} \text{ mol/L} \cdot \text{s}\end{aligned}$$

The average rates for this reaction during several other time intervals are given in Table 12.2. Note that the rate is not constant but decreases with time. The rates given in Table 12.2 are *average rates* over 50-second time intervals. The value of the rate at a particular time (the **instantaneous rate**) can be obtained by computing the slope of a line tangent to the curve at that point. Figure 12.1 shows a tangent drawn at $t = 100$ seconds. The *slope* of this line gives the rate at $t = 100$ seconds as follows:

$$\text{Slope of the tangent line} = \frac{\text{change in } y}{\text{change in } x}$$

$$= \frac{\Delta[\text{NO}_2]}{\Delta t}$$

TABLE 12.2 Average Rate (in mol/L · s) of Decomposition of Nitrogen Dioxide as a Function of Time*

$\frac{\Delta [\text{NO}_2]}{\Delta t}$	Time Period (s)
4.2×10^{-5}	0 → 50
2.8×10^{-5}	50 → 100
2.0×10^{-5}	100 → 150
1.4×10^{-5}	150 → 200
1.0×10^{-5}	200 → 250

*Note that the *rate* decreases with time.



Los Angeles on a clear day, and on a day when air pollution is significant.

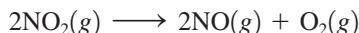
But

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t}$$

Therefore,

$$\begin{aligned}\text{Rate} &= -(\text{slope of the tangent line}) \\ &= -\left(\frac{-0.0026 \text{ mol/L}}{110 \text{ s}}\right) \\ &= 2.4 \times 10^{-5} \text{ mol/L} \cdot \text{s}\end{aligned}$$

So far we have discussed the rate of this reaction only in terms of the reactant. The rate also can be defined in terms of the products. However, in doing so we must take into account the coefficients in the balanced equation for the reaction, because the stoichiometry determines the relative rates of consumption of reactants and generation of products. For example, in the reaction we are considering,



both the reactant NO_2 and the product NO have a coefficient of 2, so NO is produced at the same rate as NO_2 is consumed. We can verify this from Fig. 12.1. Note that the curve for NO is the same shape as the curve for NO_2 , except that it is inverted, or flipped over. This means that, at any point in time, the slope of the tangent to the curve for NO will be the negative of the slope to the curve for NO_2 . (Verify this at the point $t = 100$ seconds on both curves.) In the balanced equation, the product O_2 has a coefficient of 1, which means it is produced half as fast as NO , since NO has a coefficient of 2. That is, the rate of NO production is twice the rate of O_2 production.

We also can verify this fact from Fig. 12.1. For example, at $t = 250$ seconds,

$$\begin{aligned}\text{Slope of the tangent to the NO curve} &= \frac{6.0 \times 10^{-4} \text{ mol/L}}{70. \text{ s}} \\ &= 8.6 \times 10^{-6} \text{ mol/L} \cdot \text{s} \\ \text{Slope of the tangent to the O}_2 \text{ curve} &= \frac{3.0 \times 10^{-4} \text{ mol/L}}{70. \text{ s}} \\ &= 4.3 \times 10^{-6} \text{ mol/L} \cdot \text{s}\end{aligned}$$

The slope at $t = 250$ seconds on the NO curve is twice the slope of that point on the O_2 curve, showing that the rate of production of NO is twice that of O_2 .

The rate information can be summarized as follows:

$$\begin{array}{c} \text{Rate of consumption} \\ \text{of } \text{NO}_2 \end{array} = \begin{array}{c} \text{rate of production} \\ \text{of } \text{NO} \end{array} = \begin{array}{c} 2(\text{rate of production of } \text{O}_2) \end{array}$$

$$-\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{NO}]}{\Delta t} = 2\left(\frac{\Delta[\text{O}_2]}{\Delta t}\right)$$

We have seen that the rate of a reaction is not constant, but that it changes with time. This is so because the concentrations change with time (Fig. 12.1).

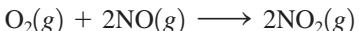
Because the reaction rate changes with time, and because the rate is different (by factors that depend on the coefficients in the balanced equation) depending on which reactant or product is being studied, we must be very specific when we describe a rate for a chemical reaction.

12.2 Rate Laws: An Introduction

Chemical reactions are *reversible*. In our discussion of the decomposition of nitrogen dioxide, we have so far considered only the *forward reaction*, as shown here:



However, the *reverse reaction* also can occur. As NO and O₂ accumulate, they can react to re-form NO₂:



When gaseous NO₂ is placed in an otherwise empty container, initially the dominant reaction is



When forward and reverse reaction rates are equal, there will be no changes in the concentrations of reactants or products. This is called *chemical equilibrium* and is discussed fully in Chapter 13.

and the change in the concentration of NO₂ ($\Delta[\text{NO}_2]$) depends only on the forward reaction. However, after a period of time, enough products accumulate so that the reverse reaction becomes important. Now $\Delta[\text{NO}_2]$ depends on the *difference in the rates of the forward and reverse reactions*. This complication can be avoided if we study the rate of a reaction under conditions where the reverse reaction makes only a negligible contribution. Typically, this means that we must study a reaction at a point soon after the reactants are mixed, before the products have had time to build up to significant levels.

If we choose conditions where the reverse reaction can be neglected, the *reaction rate will depend only on the concentrations of the reactants*. For the decomposition of nitrogen dioxide, we can write

$$\text{Rate} = k[\text{NO}_2]^n \quad (12.1)$$

Such an expression, which shows how the rate depends on the concentrations of reactants, is called a **rate law**. The proportionality constant k , called the **rate constant**, and n , called the **order** of the reactant, must both be determined by experiment. The order of a reactant can be an integer (including zero) or a fraction. For the relatively simple reactions we will consider in this book, the orders will often be positive integers.

Note two important points about Equation (12.1):

1. The concentrations of the products do not appear in the rate law because the reaction rate is being studied under conditions where the reverse reaction does not contribute to the overall rate.
2. The value of the exponent n must be determined by experiment; it cannot be written from the balanced equation.

Before we go further we must define exactly what we mean by the term *rate* in Equation (12.1). In Section 12.1 we saw that reaction rate means a change in concentration per unit time. However, which reactant or product concentration do we choose in defining the rate? For example, for the decomposition of NO_2 to produce O_2 and NO considered in Section 12.1, we could define the rate in terms of any of these three species. However, since O_2 is produced only half as fast as NO , we must be careful to specify which species we are talking about in a given case. For instance, we might choose to define the reaction rate in terms of the consumption of NO_2 :

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = k[\text{NO}_2]^n$$

On the other hand, we could define the rate in terms of the production of O_2 :

$$\text{Rate}' = \frac{\Delta[\text{O}_2]}{\Delta t} = k'[\text{NO}_2]^n$$

Note that because 2NO_2 molecules are consumed for every O_2 molecule produced,

$$\begin{aligned}\text{Rate} &= 2 \times \text{rate}' \\ \text{or} \quad k[\text{NO}_2]^n &= 2k'[\text{NO}_2]^n \\ \text{and} \quad k &= 2 \times k'\end{aligned}$$

Thus the value of the rate constant depends on how the rate is defined.

In this text we will always be careful to define exactly what is meant by the rate for a given reaction so that there will be no confusion about which specific rate constant is being used.

Types of Rate Laws

Notice that the rate law we have used to this point expresses rate as a function of concentration. For example, for the decomposition of NO_2 we have defined

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = k[\text{NO}_2]^n$$

which tells us (once we have determined the value of n) exactly how the rate depends on the concentration of the reactant, NO_2 . A rate law that expresses how the *rate depends on concentration* is technically called the **differential rate law**, but it is often simply called the **rate law**. Thus when we use the term *the rate law* in this text, we mean the expression that gives the rate as a function of concentration.

A second kind of rate law, the **integrated rate law**, also will be important in our study of kinetics. The integrated rate law expresses how the *concentrations depend on time*. Although we will not consider the details here, a given differential rate law is always related to a certain type of integrated rate law, and vice versa. That is, if we determine the differential rate law for a given reaction, we automatically know the form of the integrated rate law for the reaction. This means that once we determine experimentally either type of rate law for a reaction, we also know the other one.

Which rate law we choose to determine by experiment often depends on what types of data are easiest to collect. If we can conveniently measure how the rate changes as the concentrations are changed, we can readily determine the differential (rate/concentration) rate law. On the other hand, if it is more convenient to measure the concentration as a function of time, we can determine the form of the integrated (concentration/time) rate law. We will discuss how rate laws are actually determined in the next several sections.

Why are we interested in determining the rate law for a reaction? How does it help us? It helps us because we can work backward from the rate law to infer the steps by

The name *differential rate law* comes from a mathematical term. We will regard it simply as a label. The terms *differential rate law* and *rate law* will be used interchangeably in this text.

which the reaction occurs. Most chemical reactions do not take place in a single step but result from a series of sequential steps. To understand a chemical reaction, we must learn what these steps are. For example, a chemist who is designing an insecticide may study the reactions involved in the process of insect growth to see what type of molecule might interrupt this series of reactions. Or an industrial chemist may be trying to make a given reaction occur faster. To accomplish this, he or she must know which step is slowest, because it is that step that must be speeded up. Thus a chemist is usually not interested in a rate law for its own sake but because of what it reveals about the steps by which a reaction occurs. We will develop a process for finding the reaction steps in this chapter.

Rate Laws: A Summary

- There are two types of rate laws.
 1. The *differential rate law* (often called simply the *rate law*) shows how the rate of a reaction depends on concentrations.
 2. The *integrated rate law* shows how the concentrations of species in the reaction depend on time.
- Because we typically consider reactions only under conditions where the reverse reaction is unimportant, our rate laws will involve only concentrations of reactants.
- Because the differential and integrated rate laws for a given reaction are related in a well-defined way, the experimental determination of *either* of the rate laws is sufficient.
- Experimental convenience usually dictates which type of rate law is determined experimentally.
- Knowing the rate law for a reaction is important mainly because we can usually infer the individual steps involved in the reaction from the specific form of the rate law.

12.3 Determining the Form of the Rate Law

The first step in understanding how a given chemical reaction occurs is to determine the *form* of the rate law. That is, we need to determine experimentally the power to which each reactant concentration must be raised in the rate law. In this section we will explore ways to obtain the differential rate law for a reaction. First, we will consider the decomposition of dinitrogen pentoxide in carbon tetrachloride solution:



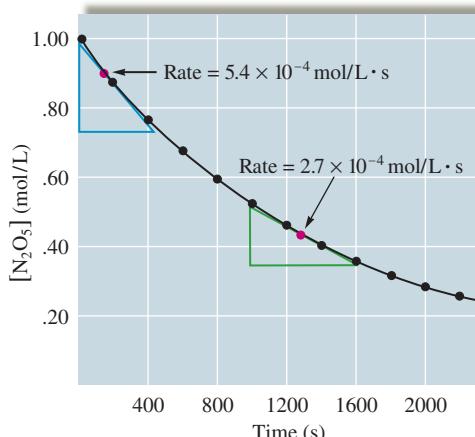
Data for this reaction at 45°C are listed in Table 12.3 and plotted in Fig. 12.3. In this reaction the oxygen gas escapes from the solution and thus does not react with the nitrogen dioxide, so we do not have to be concerned about the effects of the reverse reaction at any time over the life of the reaction. That is, the reverse reaction is negligible at all times over the course of this reaction.

Evaluation of the reaction rates at concentrations of N_2O_5 of 0.90 M and 0.45 M, by taking the slopes of the tangents to the curve at these points (see Fig. 12.3), yields the following data:

TABLE 12.3 Concentration/Time Data for the Reaction
 $2\text{N}_2\text{O}_5(\text{soln}) \rightarrow 4\text{NO}_2(\text{soln}) + \text{O}_2(\text{g})$ (at 45°C)

$[\text{N}_2\text{O}_5]$ (mol/L)	Time (s)
1.00	0
0.88	200
0.78	400
0.69	600
0.61	800
0.54	1000
0.48	1200
0.43	1400
0.38	1600
0.34	1800
0.30	2000

$[\text{N}_2\text{O}_5]$	Rate (mol/L · s)
0.90 M	5.4×10^{-4}
0.45 M	2.7×10^{-4}

**FIGURE 12.3**

A plot of the concentration of N₂O₅ as a function of time for the reaction 2N₂O₅(soln) → 4NO₂(soln) + O₂(g) (at 45°C). Note that the reaction rate at [N₂O₅] = 0.90 M is twice that at [N₂O₅] = 0.45 M.



Visualization: Decomposition of N₂O₅

First order: rate = $k[A]$. Doubling the concentration of A doubles the reaction rate.

Note that when [N₂O₅] is halved, the rate is also halved. This means that the rate of this reaction depends on the concentration of N₂O₅ to the *first power*. In other words, the (differential) rate law for this reaction is

$$\text{Rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k[\text{N}_2\text{O}_5]^1 = k[\text{N}_2\text{O}_5]$$

Thus the reaction is *first order* in N₂O₅. Note that for this reaction the order is *not* the same as the coefficient of N₂O₅ in the balanced equation for the reaction. This reemphasizes the fact that the order of a particular reactant must be obtained by *observing* how the reaction rate depends on the concentration of that reactant.

We have seen that by determining the instantaneous rate at two different reactant concentrations, the rate law for the decomposition of N₂O₅ is shown to have the form

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$$

where A represents N₂O₅.

Method of Initial Rates

The value of the initial rate is determined for each experiment at the same value of *t* as close to *t* = 0 as possible.

One common method for experimentally determining the form of the rate law for a reaction is the **method of initial rates**. The **initial rate** of a reaction is the instantaneous rate determined just after the reaction begins (just after *t* = 0). The idea is to determine the instantaneous rate before the initial concentrations of reactants have changed significantly. Several experiments are carried out using different initial concentrations, and the initial rate is determined for each run. The results are then compared to see how the initial rate depends on the initial concentrations. This allows the form of the rate law to be determined. We will illustrate the method of initial rates using the following equation:

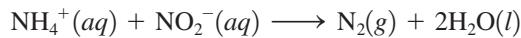


Table 12.4 gives initial rates obtained from three experiments involving different initial concentrations of reactants. The general form of the rate law for this reaction is

$$\text{Rate} = -\frac{\Delta[\text{NH}_4^+]}{\Delta t} = k[\text{NH}_4^+]^n[\text{NO}_2^-]^m$$

We can determine the values of *n* and *m* by observing how the initial rate depends on the initial concentrations of NH₄⁺ and NO₂⁻. In Experiments 1 and 2, where the initial



Visualization: Reaction Rate and Concentration

TABLE 12.4 Initial Rates from Three Experiments for the Reaction

$$\text{NH}_4^+ \text{(aq)} + \text{NO}_2^- \text{(aq)} \rightarrow \text{N}_2 \text{(g)} + 2\text{H}_2\text{O(l)}$$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate (mol/L · s)
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}

concentration of NH_4^+ remains the same but the initial concentration of NO_2^- doubles, the observed initial rate also doubles. Since

$$\text{Rate} = k[\text{NH}_4^+]^n[\text{NO}_2^-]^m$$

we have for Experiment 1

$$\text{Rate} = 1.35 \times 10^{-7} \text{ mol/L} \cdot \text{s} = k(0.100 \text{ mol/L})^n(0.0050 \text{ mol/L})^m$$

and for Experiment 2

$$\text{Rate} = 2.70 \times 10^{-7} \text{ mol/L} \cdot \text{s} = k(0.100 \text{ mol/L})^n(0.010 \text{ mol/L})^m$$

The ratio of these rates is

$$\begin{aligned} \frac{\text{Rate 2}}{\text{Rate 1}} &= \frac{2.70 \times 10^{-7} \text{ mol/L} \cdot \text{s}}{\underbrace{1.35 \times 10^{-7} \text{ mol/L} \cdot \text{s}}_{2.00}} = \frac{k(0.100 \text{ mol/L})^n(0.010 \text{ mol/L})^m}{k(0.100 \text{ mol/L})^n(0.0050 \text{ mol/L})^m} \\ &= \frac{(0.010 \text{ mol/L})^m}{(0.0050 \text{ mol/L})^m} = (2.0)^m \end{aligned}$$

Rates 1, 2, and 3 were determined at the same value of t (very close to $t = 0$).

Thus

$$\frac{\text{Rate 2}}{\text{Rate 1}} = 2.00 = (2.0)^m$$

which means the value of m is 1. The rate law for this reaction is first order in the reactant NO_2^- .

A similar analysis of the results for Experiments 2 and 3 yields the ratio

$$\begin{aligned} \frac{\text{Rate 3}}{\text{Rate 2}} &= \frac{5.40 \times 10^{-7} \text{ mol/L} \cdot \text{s}}{2.70 \times 10^{-7} \text{ mol/L} \cdot \text{s}} = \frac{(0.200 \text{ mol/L})^n}{(0.100 \text{ mol/L})^n} \\ &= 2.00 = \left(\frac{0.200}{0.100}\right)^n = (2.00)^n \end{aligned}$$

The value of n is also 1.

We have shown that the values of n and m are both 1 and the rate law is

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

This rate law is first order in both NO_2^- and NH_4^+ . Note that it is merely a coincidence that n and m have the same values as the coefficients of NH_4^+ and NO_2^- in the balanced equation for the reaction.

The **overall reaction order** is the sum of n and m . For this reaction, $n + m = 2$. The reaction is second order overall.

Overall reaction order is the sum of the orders for the various reactants.

The value of the rate constant k can now be calculated using the results of *any* of the three experiments shown in Table 12.4. From the data for Experiment 1, we know that

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

$$1.35 \times 10^{-7} \text{ mol/L} \cdot \text{s} = k(0.100 \text{ mol/L})(0.0050 \text{ mol/L})$$

Then

$$k = \frac{1.35 \times 10^{-7} \text{ mol/L} \cdot \text{s}}{(0.100 \text{ mol/L})(0.0050 \text{ mol/L})} = 2.7 \times 10^{-4} \text{ L/mol} \cdot \text{s}$$

Sample Exercise 12.1

Determining a Rate Law

The reaction between bromate ions and bromide ions in acidic aqueous solution is given by the equation

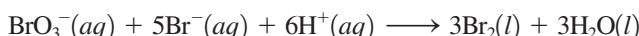


Table 12.5 gives the results from four experiments. Using these data, determine the orders for all three reactants, the overall reaction order, and the value of the rate constant.

Solution

The general form of the rate law for this reaction is

$$\text{Rate} = k[\text{BrO}_3^-]^n[\text{Br}^-]^m[\text{H}^+]^p$$

We can determine the values of n , m , and p by comparing the rates from the various experiments. To determine the value of n , we use the results from Experiments 1 and 2, in which only $[\text{BrO}_3^-]$ changes:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{1.6 \times 10^{-3} \text{ mol/L} \cdot \text{s}}{8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s}} = \frac{k(0.20 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.10 \text{ mol/L})^p}{k(0.10 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.10 \text{ mol/L})^p}$$

$$2.0 = \left(\frac{0.20 \text{ mol/L}}{0.10 \text{ mol/L}}\right)^n = (2.0)^n$$

Thus n is equal to 1.

To determine the value of m , we use the results from Experiments 2 and 3, in which only $[\text{Br}^-]$ changes:

$$\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{3.2 \times 10^{-3} \text{ mol/L} \cdot \text{s}}{1.6 \times 10^{-3} \text{ mol/L} \cdot \text{s}} = \frac{k(0.20 \text{ mol/L})^n(0.20 \text{ mol/L})^m(0.10 \text{ mol/L})^p}{k(0.20 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.10 \text{ mol/L})^p}$$

$$2.0 = \left(\frac{0.20 \text{ mol/L}}{0.10 \text{ mol/L}}\right)^m = (2.0)^m$$

Thus m is equal to 1.

TABLE 12.5 The Results from Four Experiments to Study the Reaction
 $\text{BrO}_3^-(aq) + 5\text{Br}^-(aq) + 6\text{H}^+(aq) \rightarrow 3\text{Br}_2(l) + 3\text{H}_2\text{O}(l)$

Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol/L · s)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

To determine the value of p , we use the results from Experiments 1 and 4, in which $[\text{BrO}_3^-]$ and $[\text{Br}^-]$ are constant but $[\text{H}^+]$ differs:

$$\frac{\text{Rate 4}}{\text{Rate 1}} = \frac{3.2 \times 10^{-3} \text{ mol/L} \cdot \text{s}}{8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s}} = \frac{k(0.10 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.20 \text{ mol/L})^p}{k(0.10 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.10 \text{ mol/L})^p}$$

$$4.0 = \left(\frac{0.20 \text{ mol/L}}{0.10 \text{ mol/L}}\right)^p$$

$$4.0 = (2.0)^p = (2.0)^2$$

Thus p is equal to 2.

The rate of this reaction is first order in BrO_3^- and Br^- and second order in H^+ . The overall reaction order is $n + m + p = 4$.

The rate law can now be written

$$\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

The value of the rate constant k can be calculated from the results of any of the four experiments. For Experiment 1, the initial rate is $8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s}$ and $[\text{BrO}_3^-] = 0.100 M$, $[\text{Br}^-] = 0.10 M$, and $[\text{H}^+] = 0.10 M$. Using these values in the rate law gives

$$8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s} = k(0.10 \text{ mol/L})(0.10 \text{ mol/L})(0.10 \text{ mol/L})^2$$

$$8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s} = k(1.0 \times 10^{-4} \text{ mol}^4/\text{L}^4)$$

$$k = \frac{8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s}}{1.0 \times 10^{-4} \text{ mol}^4/\text{L}^4} = 8.0 \text{ L}^3/\text{mol}^3 \cdot \text{s}$$

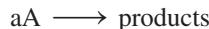
Reality Check: Verify that the same value of k can be obtained from the results of the other experiments.

See Exercises 12.25 through 12.28.

12.4 The Integrated Rate Law

The rate laws we have considered so far express the rate as a function of the reactant concentrations. It is also useful to be able to express the reactant concentrations as a function of time, given the (differential) rate law for the reaction. In this section we show how this is done.

We will proceed by first looking at reactions involving a single reactant:



all of which have a rate law of the form

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^n$$

We will develop the integrated rate laws individually for the cases $n = 1$ (first order), $n = 2$ (second order), and $n = 0$ (zero order).

First-Order Rate Laws

For the reaction



we have found that the rate law is

$$\text{Rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k[\text{N}_2\text{O}_5]$$

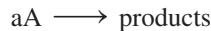
Since the rate of this reaction depends on the concentration of N_2O_5 to the first power, it is a **first-order reaction**. This means that if the concentration of N_2O_5 in a flask were suddenly doubled, the rate of production of NO_2 and O_2 also would double. This rate law can be put into a different form using a calculus operation known as integration, which yields the expression

$$\ln[\text{N}_2\text{O}_5] = -kt + \ln[\text{N}_2\text{O}_5]_0$$

Appendix 1.2 contains a review of logarithms.

where \ln indicates the natural logarithm, t is the time, $[\text{N}_2\text{O}_5]$ is the concentration of N_2O_5 at time t , and $[\text{N}_2\text{O}_5]_0$ is the initial concentration of N_2O_5 (at $t = 0$, the start of the experiment). Note that such an equation, called the *integrated rate law*, expresses the *concentration of the reactant as a function of time*.

For a chemical reaction of the form



where the kinetics are first order in $[\text{A}]$, the rate law is

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$$

and the **integrated first-order rate law** is

$$\ln[\text{A}] = -kt + \ln[\text{A}]_0 \quad (12.2)$$

There are several important things to note about Equation (12.2):

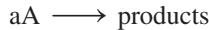
An integrated rate law relates concentration to reaction time.

1. The equation shows how the concentration of A depends on time. If the initial concentration of A and the rate constant k are known, the concentration of A at any time can be calculated.
2. Equation (12.2) is of the form $y = mx + b$, where a plot of y versus x is a straight line with slope m and intercept b . In Equation (12.2),

$$y = \ln[\text{A}] \quad x = t \quad m = -k \quad b = \ln[\text{A}]_0$$

For a first-order reaction, a plot of $\ln[\text{A}]$ versus t is always a straight line.

Thus, for a first-order reaction, plotting the natural logarithm of concentration versus time always gives a straight line. This fact is often used to test whether a reaction is first order. For the reaction



the *reaction is first order in A if a plot of $\ln[\text{A}]$ versus t is a straight line*. Conversely, if this plot is not a straight line, the reaction is not first order in A .

3. This integrated rate law for a first-order reaction also can be expressed in terms of a ratio of $[\text{A}]$ and $[\text{A}]_0$ as follows:

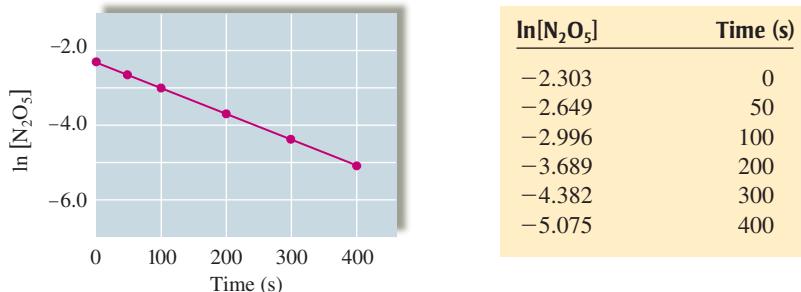
$$\ln\left(\frac{[\text{A}]_0}{[\text{A}]}\right) = kt$$

Sample Exercise 12.2

First-Order Rate Laws I

The decomposition of N_2O_5 in the gas phase was studied at constant temperature.



**FIGURE 12.4**A plot of $\ln[N_2O_5]$ versus time.

The following results were collected:

[N ₂ O ₅] (mol/L)	Time (s)
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400

Using these data, verify that the rate law is first order in [N₂O₅], and calculate the value of the rate constant, where the rate = $-\Delta[N_2O_5]/\Delta t$.

Solution

We can verify that the rate law is first order in [N₂O₅] by constructing a plot of ln[N₂O₅] versus time. The values of ln[N₂O₅] at various times are given in the table above and the plot of ln[N₂O₅] versus time is shown in Fig. 12.4. The fact that the plot is a straight line confirms that the reaction is first order in N₂O₅, since it follows the equation $\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$.

Since the reaction is first order, the slope of the line equals $-k$, where

$$\text{Slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta(\ln[N_2O_5])}{\Delta t}$$

Since the first and last points are exactly on the line, we will use these points to calculate the slope:

$$\begin{aligned}\text{Slope} &= \frac{-5.075 - (-2.303)}{400. \text{ s} - 0 \text{ s}} = \frac{-2.772}{400. \text{ s}} = -6.93 \times 10^{-3} \text{ s}^{-1} \\ k &= -(\text{slope}) = 6.93 \times 10^{-3} \text{ s}^{-1}\end{aligned}$$

See Exercise 12.31.

Sample Exercise 12.3

First-Order Rate Laws II

Using the data given in Sample Exercise 12.2, calculate [N₂O₅] at 150 s after the start of the reaction.

Solution

We know from Sample Exercise 12.2 that [N₂O₅] = 0.0500 mol/L at 100 s and [N₂O₅] = 0.0250 mol/L at 200 s. Since 150 s is halfway between 100 and 200 s, it is tempting to

assume that we can simply use an arithmetic average to obtain $[N_2O_5]$ at that time. This is incorrect because it is $\ln[N_2O_5]$, not $[N_2O_5]$, that is directly proportional to t . To calculate $[N_2O_5]$ after 150 s, we use Equation (12.2):

$$\ln[N_2O_5] = -kt + \ln[N_2O_5]_0$$

where $t = 150.$ s, $k = 6.93 \times 10^{-3} \text{ s}^{-1}$ (as determined in Sample Exercise 12.2), and $[N_2O_5]_0 = 0.1000 \text{ mol/L}$.

$$\begin{aligned}\ln([N_2O_5])_{t=150} &= -(6.93 \times 10^{-3} \text{ s}^{-1})(150. \text{ s}) + \ln(0.100) \\ &= -1.040 - 2.303 = -3.343\end{aligned}$$

$$[N_2O_5]_{t=150} = \text{antilog}(-3.343) = 0.0353 \text{ mol/L}$$

Note that this value of $[N_2O_5]$ is *not* halfway between 0.0500 and 0.0250 mol/L.

See Exercise 12.31.

The antilog operation means to exponentiate (see Appendix 1.2).



Visualization: Half-Life of Reactions

Half-Life of a First-Order Reaction

The time required for a reactant to reach half its original concentration is called the **half-life of a reactant** and is designated by the symbol $t_{1/2}$. For example, we can calculate the half-life of the decomposition reaction discussed in Sample Exercise 12.2. The data plotted in Fig. 12.5 show that the half-life for this reaction is 100 seconds. We can see this by considering the following numbers:

$[N_2O_5](\text{mol/L})$	$t (\text{s})$
0.100	0
0.0500	100 } $\Delta t = 100 \text{ s}; \frac{[N_2O_5]_{t=100}}{[N_2O_5]_{t=0}} = \frac{0.050}{0.100} = \frac{1}{2}$
0.0250	200 } $\Delta t = 100 \text{ s}; \frac{[N_2O_5]_{t=200}}{[N_2O_5]_{t=100}} = \frac{0.025}{0.050} = \frac{1}{2}$
0.0125	300 } $\Delta t = 100 \text{ s}; \frac{[N_2O_5]_{t=300}}{[N_2O_5]_{t=200}} = \frac{0.0125}{0.0250} = \frac{1}{2}$

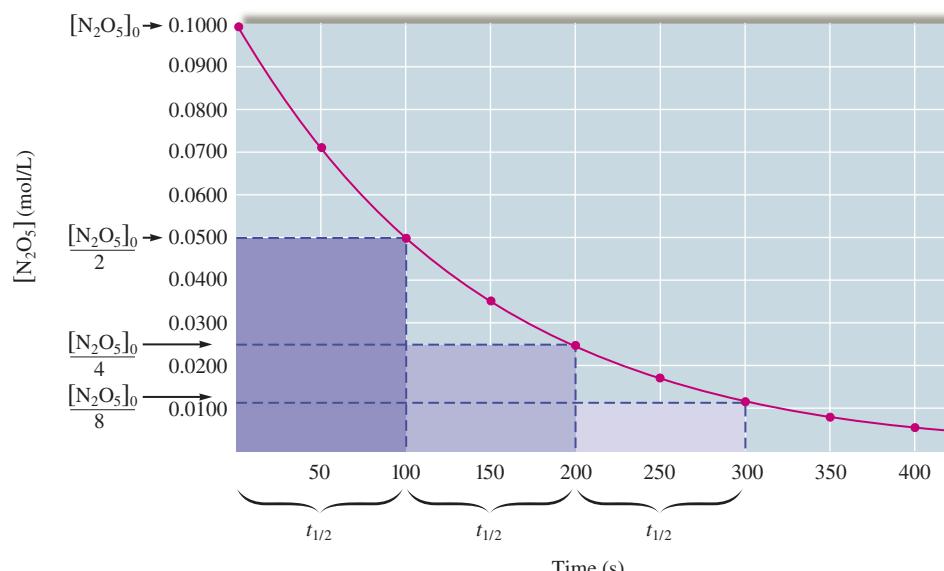
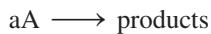


FIGURE 12.5

A plot of $[N_2O_5]$ versus time for the decomposition reaction of N_2O_5 .

Note that it *always* takes 100 seconds for $[N_2O_5]$ to be halved in this reaction.

A general formula for the half-life of a first-order reaction can be derived from the integrated rate law for the general reaction



If the reaction is first order in $[A]$,

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

By definition, when $t = t_{1/2}$,

$$[A] = \frac{[A]_0}{2}$$

Then, for $t = t_{1/2}$, the integrated rate law becomes

$$\ln\left(\frac{[A]_0}{[A]_0/2}\right) = kt_{1/2}$$

$$\text{or} \quad \ln(2) = kt_{1/2}.$$

Substituting the value of $\ln(2)$ and solving for $t_{1/2}$ gives

$$t_{1/2} = \frac{0.693}{k} \quad (12.3)$$

For a first-order reaction, $t_{1/2}$ is independent of the initial concentration.

This is the *general equation for the half-life of a first-order reaction*. Equation (12.3) can be used to calculate $t_{1/2}$ if k is known or k if $t_{1/2}$ is known. Note that for a first-order reaction, *the half-life does not depend on concentration*.

Sample Exercise 12.4

Half-Life for First-Order Reaction

A certain first-order reaction has a half-life of 20.0 minutes.

- Calculate the rate constant for this reaction.
- How much time is required for this reaction to be 75% complete?

Solution

- Solving Equation (12.3) for k gives

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20.0 \text{ min}} = 3.47 \times 10^{-2} \text{ min}^{-1}$$

- We use the integrated rate law in the form

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

If the reaction is 75% complete, 75% of the reactant has been consumed, leaving 25% in the original form:

$$\frac{[A]}{[A]_0} \times 100\% = 25\%$$

This means that

$$\frac{[A]}{[A]_0} = 0.25 \quad \text{or} \quad \frac{[A]_0}{[A]} = \frac{1}{0.25} = 4.0$$

Then

$$\ln\left(\frac{[A]_0}{[A]}\right) = \ln(4.0) = kt = \left(\frac{3.47 \times 10^{-2}}{\text{min}}\right)t$$

and

$$t = \frac{\ln(4.0)}{3.47 \times 10^{-2}} = 40. \text{ min}$$

min

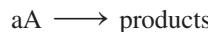
Thus it takes 40. minutes for this particular reaction to reach 75% completion.

Let's consider another way of solving this problem using the definition of half-life. After one half-life the reaction has gone 50% to completion. If the initial concentration were 1.0 mol/L, after one half-life the concentration would be 0.50 mol/L. One more half-life would produce a concentration of 0.25 mol/L. Comparing 0.25 mol/L with the original 1.0 mol/L shows that 25% of the reactant is left after two half-lives. This is a general result. (What percentage of reactant remains after three half-lives?) Two half-lives for this reaction is 2(20.0 min), or 40.0 min, which agrees with the preceding answer.

See Exercises 12.32 and 12.42 through 12.44.

Second-Order Rate Laws

For a general reaction involving a single reactant, that is,



that is second order in A, the rate law is

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2 \quad (12.4)$$

The **integrated second-order rate law** has the form

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \quad (12.5)$$

Note the following characteristics of Equation (12.5):

1. A plot of $1/[A]$ versus t will produce a straight line with a slope equal to k .
2. Equation (12.5) shows how $[A]$ depends on time and can be used to calculate $[A]$ at any time t , provided k and $[A]_0$ are known.

When one half-life of the second-order reaction has elapsed ($t = t_{1/2}$), by definition,

$$[A] = \frac{[A]_0}{2}$$

Equation (12.5) then becomes

$$\begin{aligned} \frac{1}{[A]_0} &= kt_{1/2} + \frac{1}{[A]_0} \\ \frac{2}{[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\ \frac{1}{[A]_0} &= kt_{1/2} \end{aligned}$$

Solving for $t_{1/2}$ gives the expression for the half-life of a second-order reaction:

$$t_{1/2} = \frac{1}{k[A]_0} \quad (12.6)$$

Second order: rate = $k[A]^2$. Doubling the concentration of A quadruples the reaction rate; tripling the concentration of A increases the rate by nine times.

For second-order reactions, a plot of $1/[A]$ versus t will be linear.

Sample Exercise 12.5**Determining Rate Laws**

Butadiene reacts to form its dimer according to the equation



The following data were collected for this reaction at a given temperature:

$[\text{C}_4\text{H}_6]$ (mol/L)	Time (± 1 s)
0.01000	0
0.00625	1000
0.00476	1800
0.00370	2800
0.00313	3600
0.00270	4400
0.00241	5200
0.00208	6200

- Is this reaction first order or second order?
- What is the value of the rate constant for the reaction?
- What is the half-life for the reaction under the conditions of this experiment?

Solution

- To decide whether the rate law for this reaction is first order or second order, we must see whether the plot of $\ln[\text{C}_4\text{H}_6]$ versus time is a straight line (first order) or the plot of $1/[\text{C}_4\text{H}_6]$ versus time is a straight line (second order). The data necessary to make these plots are as follows:

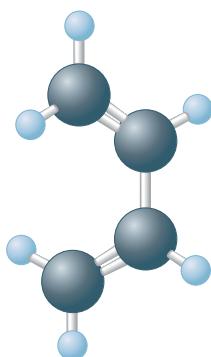
t (s)	$\frac{1}{[\text{C}_4\text{H}_6]}$	$\ln[\text{C}_4\text{H}_6]$
0	100	-4.605
1000	160	-5.075
1800	210	-5.348
2800	270	-5.599
3600	320	-5.767
4400	370	-5.915
5200	415	-6.028
6200	481	-6.175

The resulting plots are shown in Fig. 12.6. Since the $\ln[\text{C}_4\text{H}_6]$ versus t plot [Fig. 12.6(a)] is not a straight line, the reaction is *not* first order. The reaction is, however, second order, as shown by the linearity of the $1/[\text{C}_4\text{H}_6]$ versus t plot [Fig. 12.6(b)]. Thus we can now write the rate law for this second-order reaction:

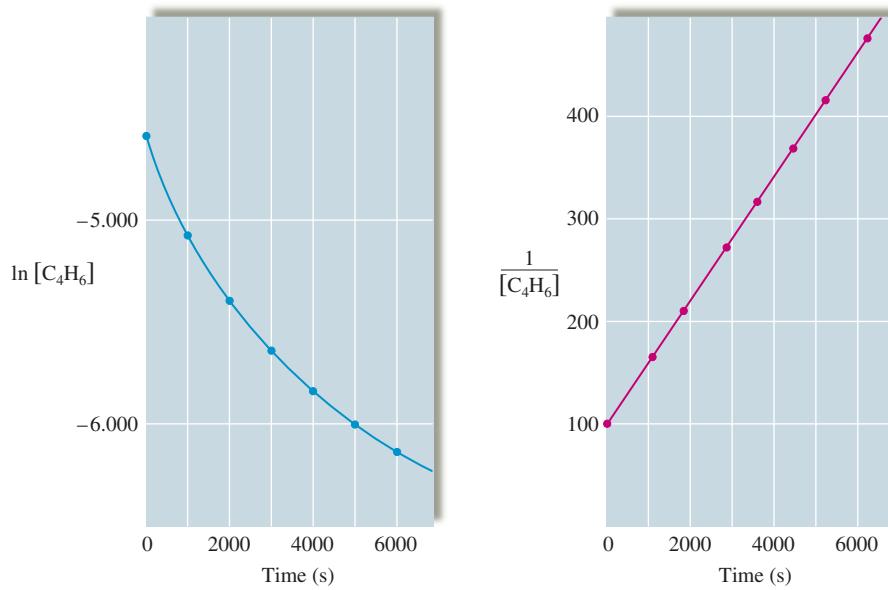
$$\text{Rate} = -\frac{\Delta[\text{C}_4\text{H}_6]}{\Delta t} = k[\text{C}_4\text{H}_6]^2$$

- For a second-order reaction, a plot of $1/[\text{C}_4\text{H}_6]$ versus t produces a straight line of slope k . In terms of the standard equation for a straight line, $y = mx + b$, we have $y = 1/[\text{C}_4\text{H}_6]$ and $x = t$. Thus the slope of the line can be expressed as follows:

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{\Delta \left(\frac{1}{[\text{C}_4\text{H}_6]} \right)}{\Delta t}$$



Butadiene (C_4H_6)

**FIGURE 12.6**

(a) A plot of $\ln[C_4H_6]$ versus t . (b) A plot of $1/[C_4H_6]$ versus t .

(a)

(b)

Using the points at $t = 0$ and $t = 6200$, we can find the rate constant for the reaction:

$$k = \text{slope} = \frac{(481 - 100) \text{ L/mol}}{(6200 - 0) \text{ s}} = \frac{381}{6200} \text{ L/mol} \cdot \text{s} = 6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s}$$

c. The expression for the half-life of a second-order reaction is

$$t_{1/2} = \frac{1}{k[A]_0}$$

In this case $k = 6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s}$ (from part b) and $[A]_0 = [C_4H_6]_0 = 0.01000 M$ (the concentration at $t = 0$). Thus

$$t_{1/2} = \frac{1}{(6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s})(1.000 \times 10^{-2} \text{ mol/L})} = 1.63 \times 10^3 \text{ s}$$

The initial concentration of C_4H_6 is halved in 1630 s.

See Exercises 12.33, 12.34, 12.45, and 12.46.

For a second-order reaction, $t_{1/2}$ is dependent on $[A]_0$. For a first-order reaction, $t_{1/2}$ is independent of $[A]_0$.

It is important to recognize the difference between the half-life for a first-order reaction and the half-life for a second-order reaction. For a second-order reaction, $t_{1/2}$ depends on both k and $[A]_0$; for a first-order reaction, $t_{1/2}$ depends only on k . For a first-order reaction, a constant time is required to reduce the concentration of the reactant by half, and then by half again, and so on, as the reaction proceeds. From Sample Exercise 12.5 we can see that this is *not* true for a second-order reaction. For that second-order reaction, we found that the first half-life (the time required to go from $[C_4H_6] = 0.010 M$ to $[C_4H_6] = 0.0050 M$) is 1630 seconds. We can estimate the second half-life from the concentration data as a function of time. Note that to reach $0.0024 M C_4H_6$ (approximately $0.0050/2$) requires 5200 seconds of reaction time. Thus to get from $0.0050 M C_4H_6$ to $0.0024 M C_4H_6$ takes 3570 seconds ($5200 - 1630$). The second half-life is much longer than the first. This pattern is characteristic of second-order reactions. In fact, *for a second-order reaction, each successive half-life is double the preceding one* (provided the effects

For each successive half-life, $[A]_0$ is halved. Since $t_{1/2} = 1/k[A]_0$, $t_{1/2}$ doubles.

of the reverse reaction can be ignored, as we are assuming here). Prove this to yourself by examining the equation $t_{1/2} = 1/(k[A]_0)$.

Zero-Order Rate Laws

Most reactions involving a single reactant show either first-order or second-order kinetics. However, sometimes such a reaction can be a **zero-order reaction**. The rate law for a zero-order reaction is

$$\text{Rate} = k[A]^0 = k(1) = k$$

A zero-order reaction has a constant rate.

For a zero-order reaction, the rate is constant. It does not change with concentration as it does for first-order or second-order reactions.

The **integrated rate law for a zero-order reaction** is

$$[A] = -kt + [A]_0 \quad (12.7)$$

In this case a plot of $[A]$ versus t gives a straight line of slope $-k$, as shown in Fig. 12.7.

The expression for the half-life of a zero-order reaction can be obtained from the integrated rate law. By definition, $[A] = [A]_0/2$ when $t = t_{1/2}$, so

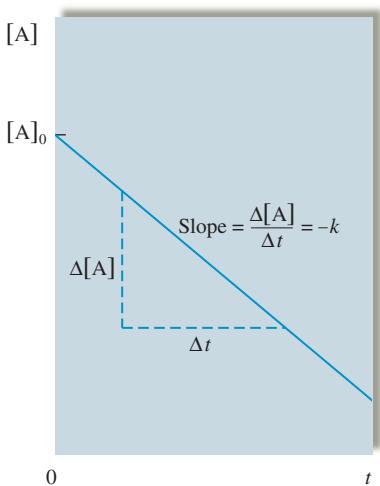
$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

$$\text{or} \quad kt_{1/2} = \frac{[A]_0}{2k}$$

Solving for $t_{1/2}$ gives

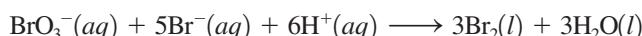
$$t_{1/2} = \frac{[A]_0}{2k} \quad (12.8)$$

Zero-order reactions are most often encountered when a substance such as a metal surface or an enzyme is required for the reaction to occur. For example, the decomposition reaction



Integrated Rate Laws for Reactions with More Than One Reactant

So far we have considered the integrated rate laws for simple reactions with only one reactant. Special techniques are required to deal with more complicated reactions. Let's consider the reaction



From experimental evidence we know that the rate law is

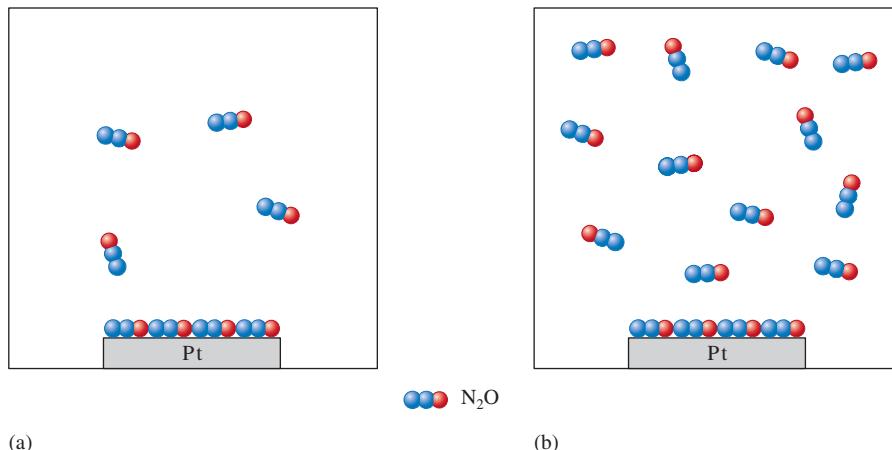
$$\text{Rate} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

FIGURE 12.7

A plot of $[A]$ versus t for a zero-order reaction.

FIGURE 12.8

The decomposition reaction $2\text{N}_2\text{O}(g) \rightarrow 2\text{N}_2(g) + \text{O}_2(g)$ takes place on a platinum surface. Although $[\text{N}_2\text{O}]$ is twice as great in (b) as in (a), the rate of decomposition of N_2O is the same in both cases because the platinum surface can accommodate only a certain number of molecules. As a result, this reaction is zero order.



Suppose we run this reaction under conditions where $[BrO_3^-]_0 = 1.0 \times 10^{-3} M$, $[Br^-]_0 = 1.0 M$, and $[H^+]_0 = 1.0 M$. As the reaction proceeds, $[BrO_3^-]$ decreases significantly, but because the Br^- ion and H^+ ion concentrations are so large initially, relatively little of these two reactants is consumed. Thus $[Br^-]$ and $[H^+]$ remain *approximately constant*. In other words, under the conditions where the Br^- ion and H^+ ion concentrations are much larger than the BrO_3^- ion concentration, we can assume that throughout the reaction

$$[\text{Br}^-] = [\text{Br}^-]_0 \quad \text{and} \quad [\text{H}^+] = [\text{H}^+]_0$$

This means that the rate law can be written

$$\text{Rate} = k[\text{Br}^-]_0 [\text{H}^+]_0^2 [\text{BrO}_3^-] = k'[\text{BrO}_3^-]$$

where, since $[Br^-]_0$ and $[H^+]_0$ are constant,

$$k' = k[\text{Br}^-]_0[\text{H}^+]_0^2$$

The rate law

$$\text{Rate} = k'[\text{BrO}_3^-]$$

is first order. However, since this law was obtained by simplifying a more complicated one, it is called a **pseudo-first-order rate law**. Under the conditions of this experiment, a plot of $\ln[\text{BrO}_3^-]$ versus t will give a straight line where the slope is equal to $-k'$. Since $[\text{Br}^-]_0$ and $[\text{H}^+]_0$ are known, the value of k can be calculated from the equation

$$k' = k[\text{Br}^-]_0[\text{H}^+]_0^2$$

which can be rearranged to give

$$k = \frac{k'}{[\text{Br}^-]_0 [\text{H}^+]_0^2}$$

Note that the kinetics of complicated reactions can be studied by observing the behavior of one reactant at a time. If the concentration of one reactant is much smaller than the concentrations of the others, then the amounts of those reactants present in large concentrations will not change significantly and can be regarded as constant. The change in concentration with time of the reactant present in a relatively small amount can then be used to determine the order of the reaction in that component. This technique allows us to determine rate laws for complex reactions.

12.5 Rate Laws: A Summary

In the last several sections we have developed the following important points:

- To simplify the rate laws for reactions, we have always assumed that the rate is being studied under conditions where only the forward reaction is important. This produces rate laws that contain only reactant concentrations.
- There are two types of rate laws.
 - The *differential rate law* (often called the *rate law*) shows how the rate depends on the concentrations. The forms of the rate laws for zero-order, first-order, and second-order kinetics of reactions with single reactants are shown in Table 12.6.
 - The *integrated rate law* shows how concentration depends on time. The integrated rate laws corresponding to zero-order, first-order, and second-order kinetics of one-reactant reactions are given in Table 12.6.
- Whether we determine the differential rate law or the integrated rate law depends on the type of data that can be collected conveniently and accurately. Once we have experimentally determined either type of rate law, we can write the other for a given reaction.
- The most common method for experimentally determining the differential rate law is the method of initial rates. In this method several experiments are run at different initial concentrations and the instantaneous rates are determined for each at the same value of t (as close to $t = 0$ as possible). The point is to evaluate the rate before the concentrations change significantly from the initial values. From a comparison of the initial rates and the initial concentrations the dependence of the rate on the concentrations of various reactants can be obtained—that is, the order in each reactant can be determined.
- To experimentally determine the integrated rate law for a reaction, concentrations are measured at various values of t as the reaction proceeds. Then the job is to see which integrated rate law correctly fits the data. Typically this is done visually by ascertaining which type of plot gives a straight line. A summary for one-reactant reactions is given in Table 12.6. Once the correct straight-line plot is found, the correct integrated rate law can be chosen and the value of k obtained from the slope. Also, the (differential) rate law for the reaction can then be written.



Visualization: Rate Laws

TABLE 12.6 Summary of the Kinetics for Reactions of the Type $aA \rightarrow$ Products That Are Zero, First, or Second Order in [A]

	Order		
	Zero	First	Second
Rate Law:	$\text{Rate} = k$	$\text{Rate} = k[\text{A}]$	$\text{Rate} = k[\text{A}]^2$
Integrated Rate Law:	$[\text{A}] = -kt + [\text{A}]_0$	$\ln[\text{A}] = -kt + \ln[\text{A}]_0$	$\frac{1}{[\text{A}]} = kt + \frac{1}{[\text{A}]_0}$
Plot Needed to Give a Straight Line: Relationship of Rate Constant to the Slope of Straight Line:	$[\text{A}]$ versus t	$\ln[\text{A}]$ versus t	$\frac{1}{[\text{A}]}$ versus t
Half-Life:	$\text{Slope} = -k$	$\text{Slope} = -k$	$\text{Slope} = k$
	$t_{1/2} = \frac{[\text{A}]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[\text{A}]_0}$

6. The integrated rate law for a reaction that involves several reactants can be treated by choosing conditions such that the concentration of only one reactant varies in a given experiment. This is done by having the concentration of one reactant remain small compared with the concentrations of all the others, causing a rate law such as

$$\text{Rate} = k[A]^n[B]^m[C]^p$$

to reduce to

$$\text{Rate} = k'[A]^n$$

where $k' = k[B]_0^m[C]_0^p$ and $[B]_0 \gg [A]_0$ and $[C]_0 \gg [A]_0$. The value of n is obtained by determining whether a plot of $[A]$ versus t is linear ($n = 0$), a plot of $\ln[A]$ versus t is linear ($n = 1$), or a plot of $1/[A]$ versus t is linear ($n = 2$). The value of k' is determined from the slope of the appropriate plot. The values of m , p , and k can be found by determining the value of k' at several different concentrations of B and C.

12.6 Reaction Mechanisms



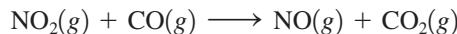
Visualization: Oscillating Reaction

A balanced equation does not tell us *how* the reactants become products.

An intermediate is formed in one step and used up in a subsequent step and so is never seen as a product.

Most chemical reactions occur by a *series of steps* called the **reaction mechanism**. To understand a reaction, we must know its mechanism, and one of the main purposes for studying kinetics is to learn as much as possible about the steps involved in a reaction. In this section we explore some of the fundamental characteristics of reaction mechanisms.

Consider the reaction between nitrogen dioxide and carbon monoxide:

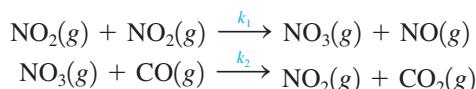


The rate law for this reaction is known from experiment to be

$$\text{Rate} = k[\text{NO}_2]^2$$

As we will see below, this reaction is more complicated than it appears from the balanced equation. This is quite typical; the balanced equation for a reaction tells us the reactants, the products, and the stoichiometry but gives no direct information about the reaction mechanism.

For the reaction between nitrogen dioxide and carbon monoxide, the mechanism is thought to involve the following steps:



where k_1 and k_2 are the rate constants of the individual reactions. In this mechanism, gaseous NO_3 is an **intermediate**, a species that is neither a reactant nor a product but that is formed and consumed during the reaction sequence. This reaction is illustrated in Fig. 12.9.

Step 1



Step 2

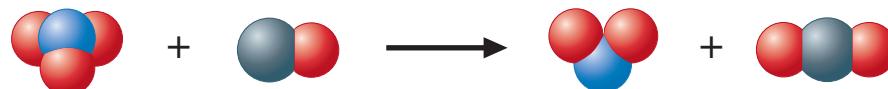


FIGURE 12.9

A molecular representation of the elementary steps in the reaction of NO_2 and CO .

TABLE 12.7 Examples of Elementary Steps

Elementary Step	Molecularity	Rate Law
$A \rightarrow \text{products}$	Unimolecular	$\text{Rate} = k[A]$
$A + A \rightarrow \text{products}$ $(2A \rightarrow \text{products})$	Bimolecular	$\text{Rate} = k[A]^2$
$A + B \rightarrow \text{products}$	Bimolecular	$\text{Rate} = k[A][B]$
$A + A + B \rightarrow \text{products}$ $(2A + B \rightarrow \text{products})$	Termolecular	$\text{Rate} = k[A]^2[B]$
$A + B + C \rightarrow \text{products}$	Termolecular	$\text{Rate} = k[A][B][C]$

The prefix *uni-* means one, *bi-* means two, and *ter-* means three.

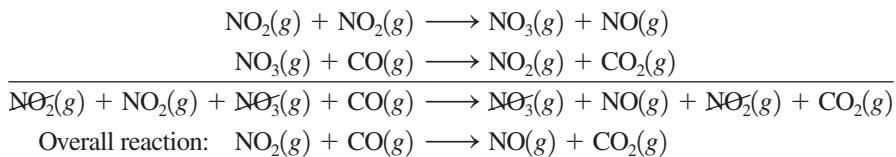
A unimolecular elementary step is always first order, a bimolecular step is always second order, and so on.

Each of these two reactions is called an **elementary step**, *a reaction whose rate law can be written from its molecularity*. **Molecularity** is defined as the number of species that must collide to produce the reaction indicated by that step. A reaction involving one molecule is called a **unimolecular step**. Reactions involving the collision of two and three species are termed **bimolecular** and **termolecular**, respectively. Termolecular steps are quite rare, because the probability of three molecules colliding simultaneously is very small. Examples of these three types of elementary steps and the corresponding rate laws are shown in Table 12.7. Note from Table 12.7 that the rate law for an elementary step follows *directly* from the molecularity of that step. For example, for a bimolecular step the rate law is always second order, either of the form $k[A]^2$ for a step with a single reactant or of the form $k[A][B]$ for a step involving two reactants.

We can now define a reaction mechanism more precisely. It is a *series of elementary steps that must satisfy two requirements*:

1. The sum of the elementary steps must give the overall balanced equation for the reaction.
2. The mechanism must agree with the experimentally determined rate law.

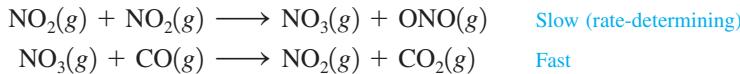
To see how these requirements are applied, we will consider the mechanism given above for the reaction of nitrogen dioxide and carbon monoxide. First, note that the sum of the two steps gives the overall balanced equation:



A reaction is only as fast as its slowest step.

The first requirement for a correct mechanism is met. To see whether the mechanism meets the second requirement, we need to introduce a new idea: the **rate-determining step**. Multistep reactions often have one step that is much slower than all the others. Reactants can become products only as fast as they can get through this slowest step. That is, the overall reaction can be no faster than the slowest, or rate-determining, step in the sequence. An analogy for this situation is the pouring of water rapidly into a container through a funnel. The water collects in the container at a rate that is essentially determined by the size of the funnel opening and not by the rate of pouring.

Which is the rate-determining step in the reaction of nitrogen dioxide and carbon monoxide? Let's *assume* that the first step is rate-determining and the second step is relatively fast:



What we have really assumed here is that the formation of NO_3 occurs much more slowly than its reaction with CO . The rate of CO_2 production is then controlled by the rate of formation of NO_3 in the first step. Since this is an elementary step, we can write the rate law from the molecularity. The bimolecular first step has the rate law

$$\text{Rate of formation of } \text{NO}_3 = \frac{\Delta[\text{NO}_3]}{\Delta t} = k_1[\text{NO}_2]^2$$

Since the overall reaction rate can be no faster than the slowest step,

$$\text{Overall rate} = k_1[\text{NO}_2]^2$$

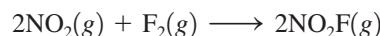
Note that this rate law agrees with the experimentally determined rate law given earlier. The mechanism we assumed above satisfies the two requirements stated earlier and *may* be the correct mechanism for the reaction.

How does a chemist deduce the mechanism for a given reaction? The rate law is always determined first. Then, using chemical intuition and following the two rules given on the previous page, the chemist constructs possible mechanisms and tries, with further experiments, to eliminate those that are least likely. A mechanism *can never be proved absolutely*. We can only say that a mechanism that satisfies the two requirements is *possibly* correct. Deducing mechanisms for chemical reactions can be difficult and requires skill and experience. We will only touch on this process in this text.

Sample Exercise 12.6

Reaction Mechanisms

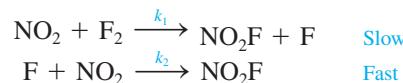
The balanced equation for the reaction of the gases nitrogen dioxide and fluorine is



The experimentally determined rate law is

$$\text{Rate} = k[\text{NO}_2][\text{F}_2]$$

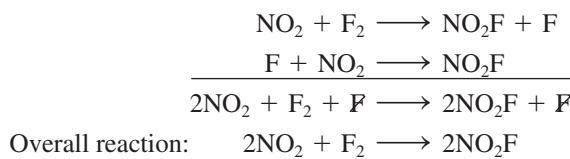
A suggested mechanism for this reaction is



Is this an acceptable mechanism? That is, does it satisfy the two requirements?

Solution

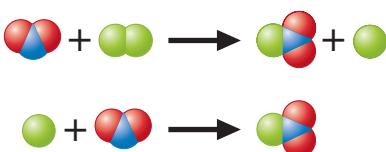
The first requirement for an acceptable mechanism is that the sum of the steps should give the balanced equation:



The first requirement is met.

The second requirement is that the mechanism must agree with the experimentally determined rate law. Since the proposed mechanism states that the first step is rate-determining, the overall reaction rate must be that of the first step. The first step is bimolecular, so the rate law is

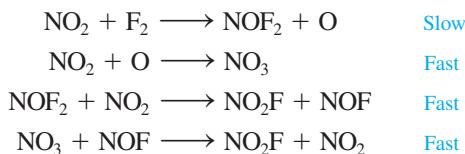
$$\text{Rate} = k_1[\text{NO}_2][\text{F}_2]$$



This has the same form as the experimentally determined rate law. The proposed mechanism is acceptable because it satisfies both requirements. (Note that we have not proved that it is *the correct mechanism*.)

See Exercises 12.51 and 12.52.

Although the mechanism given in Sample Exercise 12.6 has the correct stoichiometry and fits the observed rate law, other mechanisms may also satisfy these requirements. For example, the mechanism might be



To decide on the most probable mechanism for the reaction, the chemist doing the study would have to perform additional experiments.

12.7 A Model for Chemical Kinetics

How do chemical reactions occur? We already have given some indications. For example, we have seen that the rates of chemical reactions depend on the concentrations of the reacting species. The initial rate for the reaction



can be described by the rate law

$$\text{Rate} = k[\text{A}]^n[\text{B}]^m$$

where the order of each reactant depends on the detailed reaction mechanism. This explains why reaction rates depend on concentration. But what about some of the other factors affecting reaction rates? For example, how does temperature affect the speed of a reaction?

We can answer this question qualitatively from our experience. We have refrigerators because food spoilage is retarded at low temperatures. The combustion of wood occurs at a measurable rate only at high temperatures. An egg cooks in boiling water much faster at sea level than in Leadville, Colorado (elevation 10,000 ft), where the boiling point of water is approximately 90°C. These observations and others lead us to conclude that *chemical reactions speed up when the temperature is increased*. Experiments have shown that virtually all rate constants show an exponential increase with absolute temperature, as represented in Fig. 12.10.

In this section we discuss a model used to account for the observed characteristics of reaction rates. This model, called the **collision model**, is built around the central idea that *molecules must collide to react*. We have already seen how this assumption explains the concentration dependence of reaction rates. Now we need to consider whether this model can account for the observed temperature dependence of reaction rates.

The kinetic molecular theory of gases predicts that an increase in temperature raises molecular velocities and so increases the frequency of collisions between molecules. This idea agrees with the observation that reaction rates are greater at higher temperatures. Thus there is qualitative agreement between the collision model and experimental observations. However, it is found that the rate of reaction is much smaller than the calculated collision frequency in a collection of gas particles. This must mean that *only a small fraction of the collisions produces a reaction*. Why?

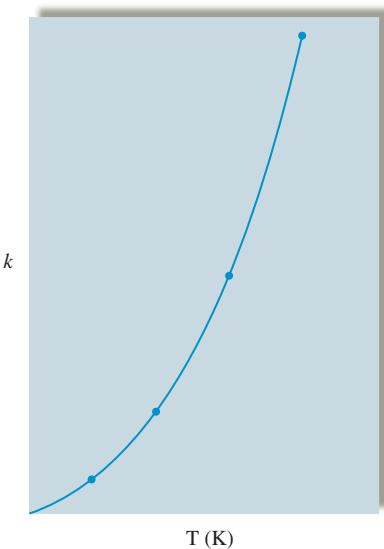
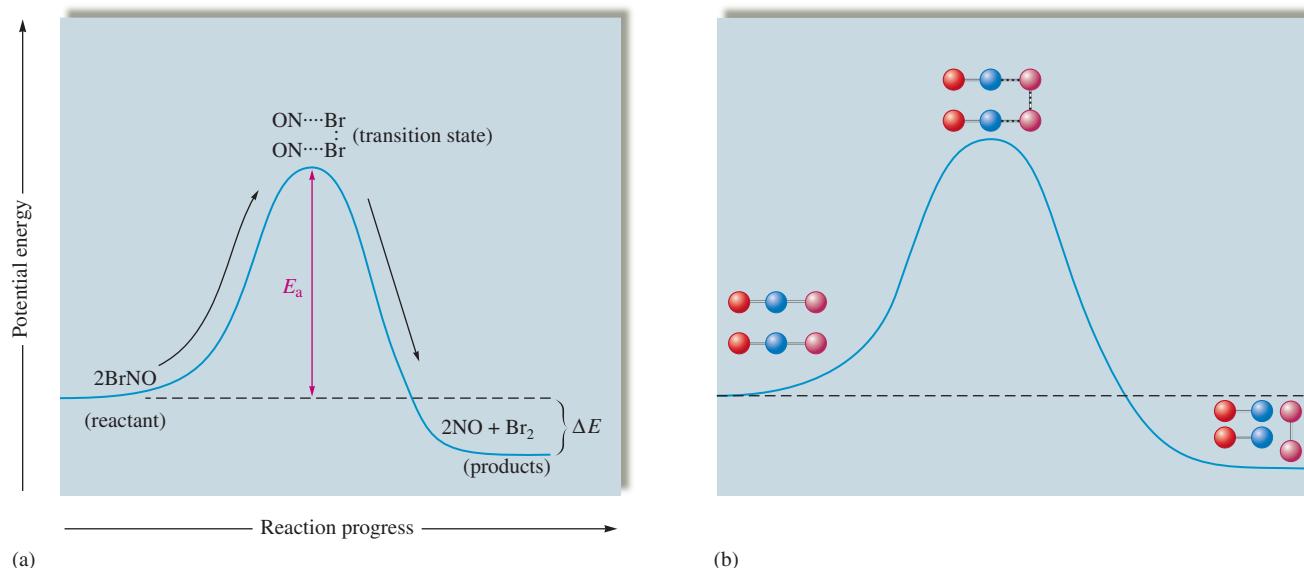


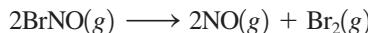
FIGURE 12.10

A plot showing the exponential dependence of the rate constant on absolute temperature. The exact temperature dependence of k is different for each reaction. This plot represents the behavior of a rate constant that doubles for every increase in temperature of 10 K.

**FIGURE 12.11**

(a) The change in potential energy as a function of reaction progress for the reaction $2\text{BrNO} \rightarrow 2\text{NO} + \text{Br}_2$. The activation energy E_a represents the energy needed to disrupt the BrNO molecules so that they can form products. The quantity ΔE represents the net change in energy in going from reactant to products. (b) A molecular representation of the reaction.

This question was first addressed in the 1880s by Svante Arrhenius. He proposed the existence of a *threshold energy*, called the **activation energy**, that must be overcome to produce a chemical reaction. Such a proposal makes sense, as we can see by considering the decomposition of BrNO in the gas phase:



In this reaction two Br—N bonds must be broken and one Br—Br bond must be formed. Breaking a Br—N bond requires considerable energy (243 kJ/mol), which must come from somewhere. The collision model postulates that the energy comes from the kinetic energies possessed by the reacting molecules before the collision. This kinetic energy is changed into potential energy as the molecules are distorted during a collision to break bonds and rearrange the atoms into the product molecules.

We can envision the reaction progress as shown in Fig. 12.11. The arrangement of atoms found at the top of the potential energy “hill,” or barrier, is called the **activated complex**, or **transition state**. The conversion of BrNO to NO and Br₂ is exothermic, as indicated by the fact that the products have lower potential energy than the reactant. However, ΔE has no effect on the rate of the reaction. Rather, the rate depends on the size of the activation energy E_a .

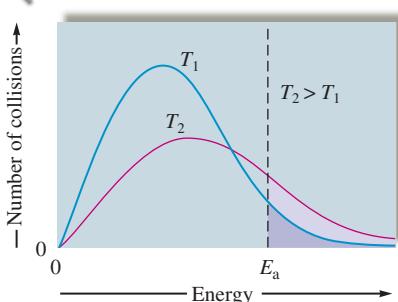
The main point here is that a certain minimum energy is required for two BrNO molecules to “get over the hill” so that products can form. This energy is furnished by the energy of the collision. A collision between two BrNO molecules with small kinetic energies will not have enough energy to get over the barrier. At a given temperature only a certain fraction of the collisions possesses enough energy to be effective (to result in product formation).

We can be more precise by recalling from Chapter 5 that a distribution of velocities exists in a sample of gas molecules. Therefore, a distribution of collision energies also exists, as shown in Fig. 12.12 for two different temperatures. Figure 12.12 also shows the activation energy for the reaction in question. Only collisions with energy greater than



Visualization: Transition States and Activation Energy

The higher the activation energy, the slower the reaction at a given temperature.

**FIGURE 12.12**

Plot showing the number of collisions with a particular energy at T_1 and T_2 , where $T_2 > T_1$.

the activation energy are able to react (get over the barrier). At the lower temperature, T_1 , the fraction of effective collisions is quite small. However, as the temperature is increased to T_2 , the fraction of collisions with the required activation energy increases dramatically. When the temperature is doubled, the fraction of effective collisions much more than doubles. In fact, the fraction of effective collisions increases *exponentially* with temperature. This is encouraging for our theory; remember that rates of reactions are observed to increase exponentially with temperature. Arrhenius postulated that the number of collisions having an energy greater than or equal to the activation energy is given by the expression:

$$\text{Number of collisions with the activation energy} = (\text{total number of collisions})e^{-E_a/RT}$$

where E_a is the activation energy, R is the universal gas constant, and T is the Kelvin temperature. The factor $e^{-E_a/RT}$ represents the fraction of collisions with energy E_a or greater at temperature T .

We have seen that not all molecular collisions are effective in producing chemical reactions because a minimum energy is required for the reaction to occur. There is, however, another complication. Experiments show that the *observed reaction rate is considerably smaller than the rate of collisions with enough energy to surmount the barrier*. This means that many collisions, even though they have the required energy, still do not produce a reaction. Why not?

The answer lies in the **molecular orientations** during collisions. We can illustrate this using the reaction between two BrNO molecules, as shown in Fig. 12.13. Some collision orientations can lead to reaction, and others cannot. Therefore, we must include a correction factor to allow for collisions with nonproductive molecular orientations.

To summarize, two requirements must be satisfied for reactants to collide successfully (to rearrange to form products):

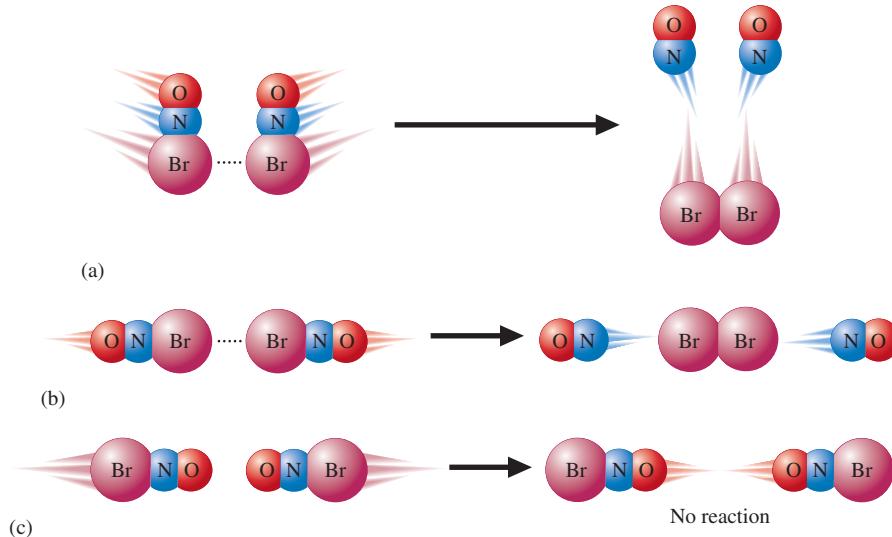
1. The collision must involve enough energy to produce the reaction; that is, the collision energy must equal or exceed the activation energy.
2. The relative orientation of the reactants must allow formation of any new bonds necessary to produce products.

Taking these factors into account, we can represent the rate constant as

$$k = zpe^{-E_a/RT}$$



Visualization: The Gas Phase Reaction of NO and Cl₂

**FIGURE 12.13**

Several possible orientations for a collision between two BrNO molecules. Orientations (a) and (b) can lead to a reaction, but orientation (c) cannot.

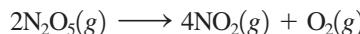


A snowy tree cricket. The frequency of a cricket's chirps depends on the temperature of the cricket.

Sample Exercise 12.7

Determining Activation Energy I

The reaction



was studied at several temperatures, and the following values of k were obtained:

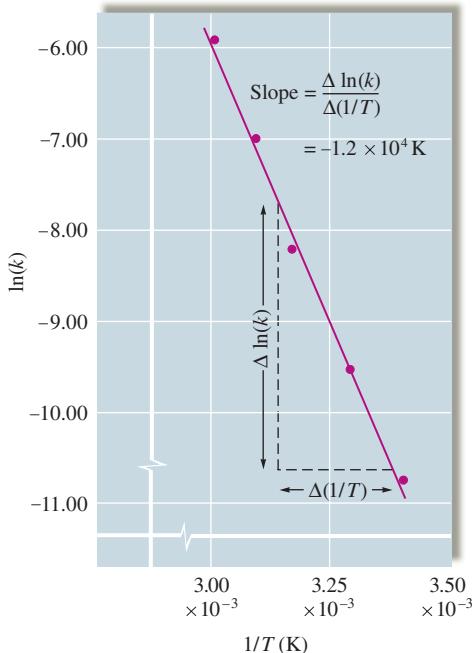
$k (\text{s}^{-1})$	$T (\text{°C})$
2.0×10^{-5}	20
7.3×10^{-5}	30
2.7×10^{-4}	40
9.1×10^{-4}	50
2.9×10^{-3}	60

Calculate the value of E_a for this reaction.

Solution

To obtain the value of E_a , we need to construct a plot of $\ln(k)$ versus $1/T$. First, we must calculate values of $\ln(k)$ and $1/T$, as shown below:

$T (\text{°C})$	$T (\text{K})$	$1/T (\text{K})$	$k (\text{s}^{-1})$	$\ln(k)$
20	293	3.41×10^{-3}	2.0×10^{-5}	-10.82
30	303	3.30×10^{-3}	7.3×10^{-5}	-9.53
40	313	3.19×10^{-3}	2.7×10^{-4}	-8.22
50	323	3.10×10^{-3}	9.1×10^{-4}	-7.00
60	333	3.00×10^{-3}	2.9×10^{-3}	-5.84

**FIGURE 12.14**

Plot of $\ln(k)$ versus $1/T$ for the reaction $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$. The value of the activation energy for this reaction can be obtained from the slope of the line, which equals $-E_a/R$.

The plot of $\ln(k)$ versus $1/T$ is shown in Fig. 12.14, where the slope

$$\frac{\Delta \ln(k)}{\Delta \left(\frac{1}{T} \right)}$$

is found to be $-1.2 \times 10^4 \text{ K}$. The value of E_a can be determined by solving the following equation:

$$\text{Slope} = -\frac{E_a}{R}$$

$$\begin{aligned} E_a &= -R(\text{slope}) = -(8.3145 \text{ J/K} \cdot \text{mol})(-1.2 \times 10^4 \text{ K}) \\ &= 1.0 \times 10^5 \text{ J/mol} \end{aligned}$$

Thus the value of the activation energy for this reaction is $1.0 \times 10^5 \text{ J/mol}$.

See Exercises 12.57 and 12.58.

The most common procedure for finding E_a for a reaction involves measuring the rate constant k at several temperatures and then plotting $\ln(k)$ versus $1/T$, as shown in Sample Exercise 12.7. However, E_a also can be calculated from the values of k at only two temperatures by using a formula that can be derived as follows from Equation (12.10).

At temperature T_1 , where the rate constant is k_1 ,

$$\ln(k_1) = -\frac{E_a}{RT_1} + \ln(A)$$

At temperature T_2 , where the rate constant is k_2 ,

$$\ln(k_2) = -\frac{E_a}{RT_2} + \ln(A)$$

Subtracting the first equation from the second gives

$$\begin{aligned}\ln(k_2) - \ln(k_1) &= \left[-\frac{E_a}{RT_2} + \ln(A) \right] - \left[-\frac{E_a}{RT_1} + \ln(A) \right] \\ &= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1} \\ \text{And } \ln\left(\frac{k_2}{k_1}\right) &= \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)\end{aligned}\quad (12.11)$$

Therefore, the values of k_1 and k_2 measured at temperatures T_1 and T_2 can be used to calculate E_a , as shown in Sample Exercise 12.8.

Sample Exercise 12.8

Determining Activation Energy II

The gas-phase reaction between methane and diatomic sulfur is given by the equation



At 550°C the rate constant for this reaction is 1.1 L/mol · s, and at 625°C the rate constant is 6.4 L/mol · s. Using these values, calculate E_a for this reaction.

Solution

The relevant data are shown in the following table:

k (L/mol · s)	T (°C)	T (K)
$1.1 = k_1$	550	$823 = T_1$
$6.4 = k_2$	625	$625 = T_2$

Substituting these values into Equation (12.11) gives

$$\ln\left(\frac{6.4}{1.1}\right) = \frac{E_a}{8.3145 \text{ J/K} \cdot \text{mol}} \left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}} \right)$$

Solving for E_a gives

$$\begin{aligned}E_a &= \frac{(8.3145 \text{ J/K} \cdot \text{mol}) \ln\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}} \right)} \\ &= 1.4 \times 10^5 \text{ J/mol}\end{aligned}$$

See Exercises 12.59 through 12.62.

12.8 Catalysis

We have seen that the rate of a reaction increases dramatically with temperature. If a particular reaction does not occur fast enough at normal temperatures, we can speed it up by raising the temperature. However, sometimes this is not feasible. For example, living cells can survive only in a rather narrow temperature range, and the human body is designed to operate at an almost constant temperature of 98.6°F. But many of the complicated biochemical reactions keeping us alive would be much too slow at this temperature without intervention. We exist only because the body contains many substances called **enzymes**, which increase the rates of these reactions. In fact, almost every biologically important reaction is assisted by a specific enzyme.

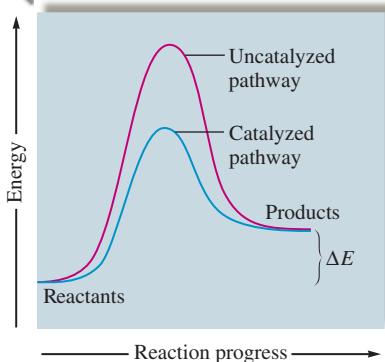


FIGURE 12.15

Energy plots for a catalyzed and an uncatalyzed pathway for a given reaction.

Although it is possible to use higher temperatures to speed up commercially important reactions, such as the Haber process for synthesizing ammonia, this is very expensive. In a chemical plant an increase in temperature means significantly increased costs for energy. The use of an appropriate catalyst allows a reaction to proceed rapidly at a relatively low temperature and can therefore hold down production costs.

A **catalyst** is a substance that speeds up a reaction without being consumed itself. Just as virtually all vital biologic reactions are assisted by enzymes (biologic catalysts), almost all industrial processes also involve the use of catalysts. For example, the production of sulfuric acid uses vanadium(V) oxide, and the Haber process uses a mixture of iron and iron oxide.

How does a catalyst work? Remember that for each reaction a certain energy barrier must be surmounted. How can we make a reaction occur faster without raising the temperature to increase the molecular energies? The solution is to provide a new pathway for the reaction, one with a *lower activation energy*. This is what a catalyst does, as is shown in Fig. 12.15. Because the catalyst allows the reaction to occur with a lower activation energy, a much larger fraction of collisions is effective at a given temperature, and the reaction rate is increased. This effect is illustrated in Fig. 12.16. Note from this diagram that although a catalyst lowers the activation energy E_a for a reaction, it does not affect the energy difference ΔE between products and reactants.

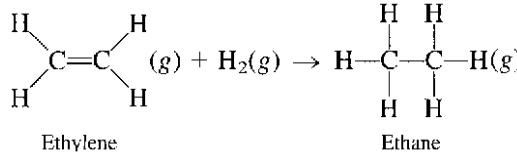
Catalysts are classified as homogeneous or heterogeneous. A **homogeneous catalyst** is one that is *present in the same phase as the reacting molecules*. A **heterogeneous catalyst** exists in a different phase, usually as a solid.

Heterogeneous Catalysis

Heterogeneous catalysis most often involves gaseous reactants being adsorbed on the surface of a solid catalyst. **Adsorption** refers to the collection of one substance on the surface of another substance; *absorption* refers to the penetration of one substance into another. Water is *absorbed* by a sponge.

An important example of heterogeneous catalysis occurs in the hydrogenation of unsaturated hydrocarbons, compounds composed mainly of carbon and hydrogen with some carbon–carbon double bonds. Hydrogenation is an important industrial process used to change unsaturated fats, occurring as oils, to saturated fats (solid shortenings such as Crisco) in which the C=C bonds have been converted to C—C bonds through addition of hydrogen.

A simple example of hydrogenation involves ethylene:

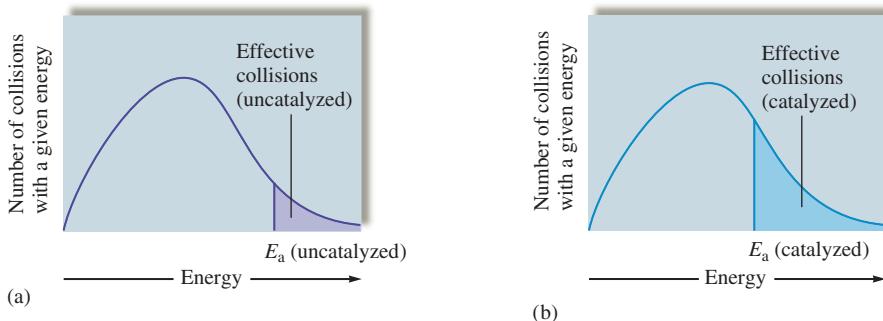


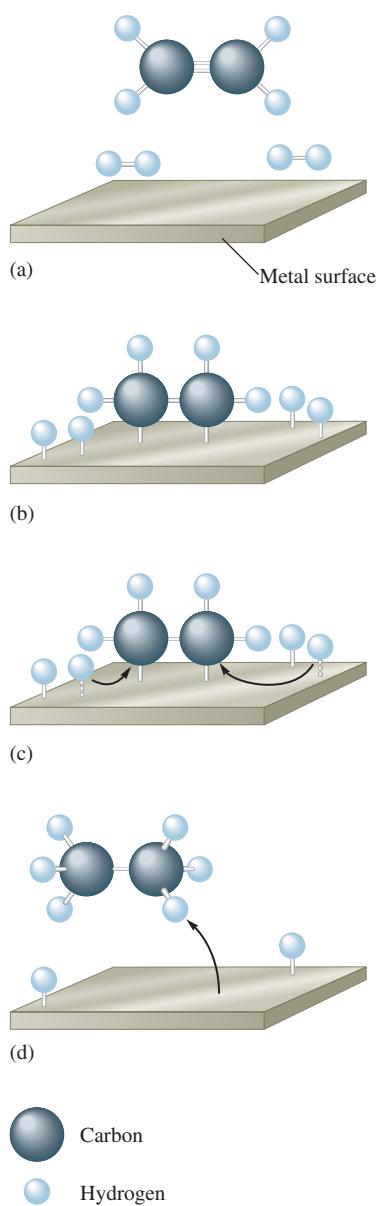
This reaction is quite slow at normal temperatures, mainly because the strong bond in the hydrogen molecule results in a large activation energy for the reaction. However, the

These cookies contain partially hydrogenated vegetable oil.

FIGURE 12-16

Effect of a catalyst on the number of reaction-producing collisions. Because a catalyst provides a reaction pathway with a lower activation energy, a much greater fraction of the collisions is effective for the catalyzed pathway (b) than for the uncatalyzed pathway (a) (at a given temperature). This allows reactants to become products at a much higher rate, even though there is no temperature increase.



**FIGURE 12.17**

Heterogeneous catalysis of the hydrogenation of ethylene. (a) The reactants above the metal surface. (b) Hydrogen is adsorbed onto the metal surface, forming metal–hydrogen bonds and breaking the H–H bonds. The π bond in ethylene is broken and metal–carbon bonds are formed during adsorption. (c) The adsorbed molecules and atoms migrate toward each other on the metal surface, forming new C–H bonds. (d) The C atoms in ethane (C_2H_6) have completely saturated bonding capacities and so cannot bind strongly to the metal surfaces. The C_2H_6 molecule thus escapes.

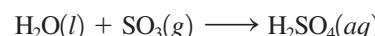
reaction rate can be greatly increased by using a solid catalyst of platinum, palladium, or nickel. The hydrogen and ethylene adsorb on the catalyst surface, where the reaction occurs. The main function of the catalyst apparently is to allow formation of metal–hydrogen interactions that weaken the H–H bonds and facilitate the reaction. The mechanism is illustrated in Fig. 12.17.

Typically, heterogeneous catalysis involves four steps:

1. Adsorption and activation of the reactants
2. Migration of the adsorbed reactants on the surface
3. Reaction of the adsorbed substances
4. Escape, or *desorption*, of the products

Heterogeneous catalysis also occurs in the oxidation of gaseous sulfur dioxide to gaseous sulfur trioxide. This process is especially interesting because it illustrates both positive and negative consequences of chemical catalysis.

The negative side is the formation of damaging air pollutants. Recall that sulfur dioxide, a toxic gas with a choking odor, is formed whenever sulfur-containing fuels are burned. However, it is sulfur trioxide that causes most of the environmental damage, mainly through the production of acid rain. When sulfur trioxide combines with a droplet of water, sulfuric acid is formed:



This sulfuric acid can cause considerable damage to vegetation, buildings and statues, and fish populations.

Sulfur dioxide is *not* rapidly oxidized to sulfur trioxide in clean, dry air. Why, then, is there a problem? The answer is catalysis. Dust particles and water droplets catalyze the reaction between SO_2 and O_2 in the air.

On the positive side, the heterogeneous catalysis of the oxidation of SO_2 is used to advantage in the manufacture of sulfuric acid, where the reaction of O_2 and SO_2 to form SO_3 is catalyzed by a solid mixture of platinum and vanadium(V) oxide.

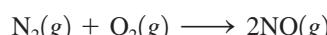
Heterogeneous catalysis is also utilized in the catalytic converters in automobile exhaust systems. The exhaust gases, containing compounds such as nitric oxide, carbon monoxide, and unburned hydrocarbons, are passed through a converter containing beads of solid catalyst (see Fig. 12.18). The catalyst promotes the conversion of carbon monoxide to carbon dioxide, hydrocarbons to carbon dioxide and water, and nitric oxide to nitrogen gas to lessen the environmental impact of the exhaust gases. However, this beneficial catalysis can, unfortunately, be accompanied by the unwanted catalysis of the oxidation of SO_2 to SO_3 , which reacts with the moisture present to form sulfuric acid.

Because of the complex nature of the reactions that take place in the converter, a mixture of catalysts is used. The most effective catalytic materials are transition metal oxides and noble metals such as palladium and platinum.

Homogeneous Catalysis

A homogeneous catalyst exists in the same phase as the reacting molecules. There are many examples in both the gas and liquid phases. One such example is the unusual catalytic behavior of nitric oxide toward ozone. In the troposphere, that part of the atmosphere closest to earth, nitric oxide catalyzes ozone production. However, in the upper atmosphere it catalyzes the decomposition of ozone. Both these effects are unfortunate environmentally.

In the lower atmosphere, NO is produced in any high-temperature combustion process where N_2 is present. The reaction





CHEMICAL IMPACT

Automobiles: Air Purifiers?

Outlandish as it may seem, a new scheme has been proposed to turn automobiles into air purifiers, devouring the pollutants ozone and carbon monoxide. Engelhard Corporation, an Iselin, New Jersey, company that specializes in the manufacture of catalytic converters for automotive exhaust systems, has developed a catalyst that decomposes ozone to oxygen and converts carbon monoxide to carbon dioxide. Engelhard proposes to paint the catalyst on auto-

mobile radiators and air-conditioner compressors where fans draw large volumes of air for cooling purposes. The catalyst works well at the warm temperatures present on the surfaces of these devices. The idea is to let cars destroy pollutants using nothing but the catalyst and waste radiator heat.

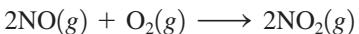
It's an intriguing idea. The residents of Los Angeles drive nearly 300 million miles every day. At that rate, they could process a lot of air.



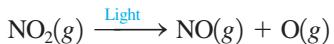
Visualization: Homogeneous Catalysis

Although O_2 is represented here as the oxidizing agent for NO, the actual oxidizing agent is probably some type of peroxide compound produced by reaction of oxygen with pollutants. The direct reaction of NO and O_2 is very slow.

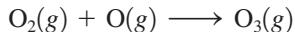
is very slow at normal temperatures because of the very strong $N\equiv N$ and $O=O$ bonds. However, at elevated temperatures, such as those found in the internal combustion engines of automobiles, significant quantities of NO form. Some of this NO is converted back to N_2 in the catalytic converter, but significant amounts escape into the atmosphere to react with oxygen:



In the atmosphere, NO_2 can absorb light and decompose as follows:



The oxygen atom is very reactive and can combine with oxygen molecules to form ozone:



Ozone is a powerful oxidizing agent that can react with other air pollutants to form substances irritating to the eyes and lungs, and is itself very toxic.

In this series of reactions, nitric oxide is acting as a true catalyst because it assists the production of ozone without being consumed itself. This can be seen by summing the reactions:

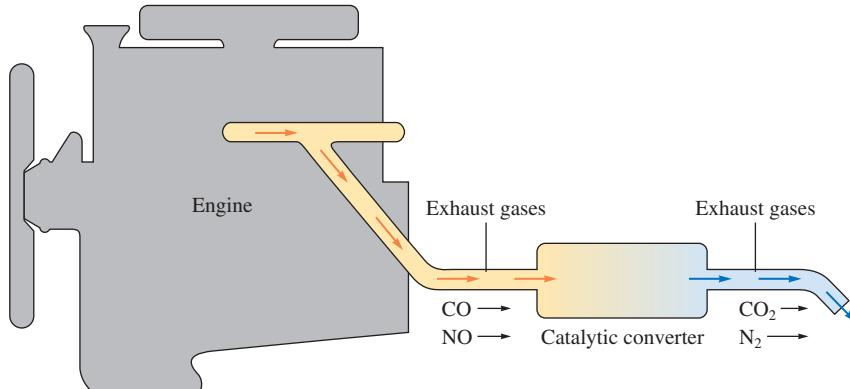
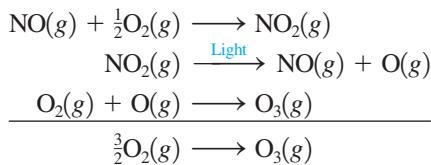
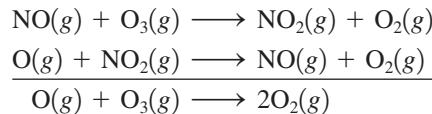


FIGURE 12.18

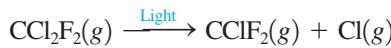
The exhaust gases from an automobile engine are passed through a catalytic converter to minimize environmental damage.

In the upper atmosphere, the presence of nitric oxide has the opposite effect—the depletion of ozone. The series of reactions involved is

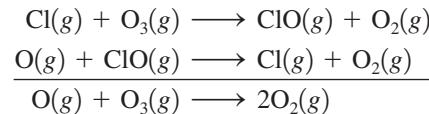


Nitric oxide is again catalytic, but here its effect is to change O_3 to O_2 . This is a potential problem because O_3 , which absorbs ultraviolet light, is necessary to protect us from the harmful effects of this high-energy radiation. That is, we want O_3 in the upper atmosphere to block ultraviolet radiation from the sun but not in the lower atmosphere, where we would have to breathe it and its oxidation products.

The ozone layer is also threatened by *Freons*, a group of stable, noncorrosive compounds, until recently, used as refrigerants and as propellants in aerosol cans. The most commonly used substance of this type was Freon-12 (CCl_2F_2). The chemical inertness of Freons makes them valuable but also creates a problem, since they remain in the environment a long time. Eventually, they migrate into the upper atmosphere to be decomposed by high-energy light. Among the decomposition products are chlorine atoms:



These chlorine atoms can catalyze the decomposition of ozone:



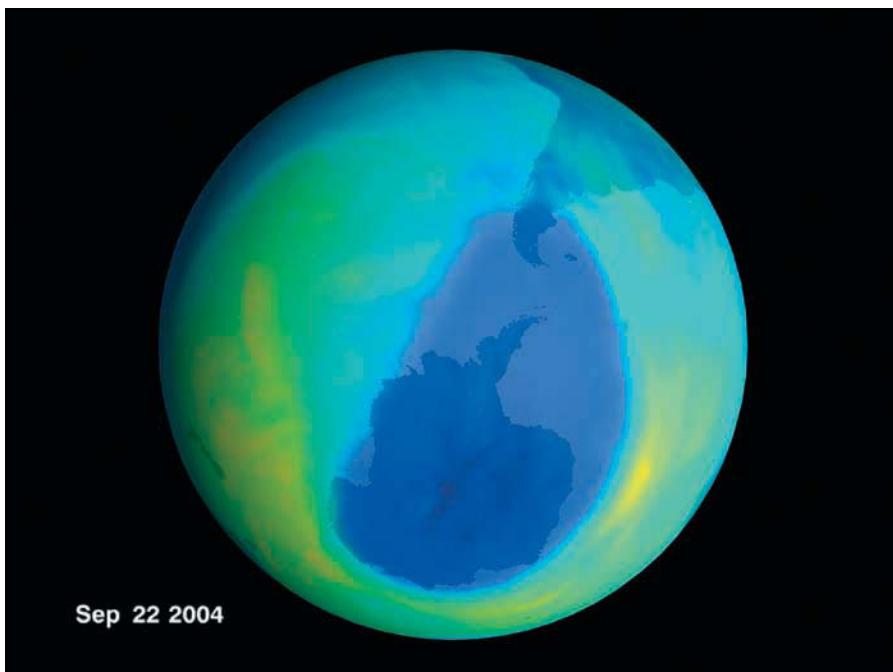
Freon-12



Ozone

The problem of Freons has been brought into strong focus by the discovery of a mysterious “hole” in the ozone layer in the stratosphere over Antarctica. Studies performed there to find the reason for the hole have found unusually high levels of chlorine monoxide (ClO). This strongly implicates the Freons in the atmosphere as being responsible for the ozone destruction.

Because they pose environmental problems, Freons have been banned by international agreement. Substitute compounds are now being used.



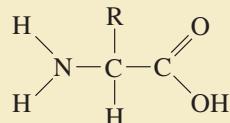
This graphic shows data from the Total Ozone Mapping Spectrometer (TOMS) Earth Probe.



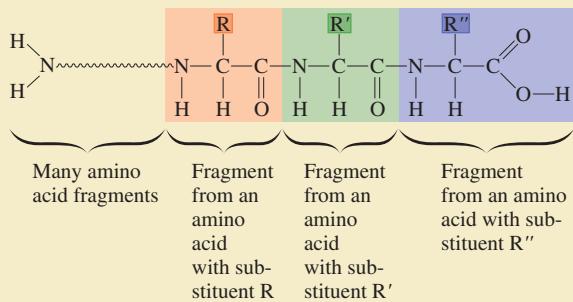
CHEMICAL IMPACT

Enzymes: Nature's Catalysts

The most impressive examples of homogeneous catalysis occur in nature, where the complex reactions necessary for plant and animal life are made possible by enzymes. Enzymes are large molecules specifically tailored to facilitate a given type of reaction. Usually enzymes are proteins, an important class of biomolecules constructed from α -amino acids that have the general structure



where R represents any one of 20 different substituents. These amino acid molecules can be “hooked together” to form a *polymer* (a word meaning “many parts”) called a *protein*. The general structure of a protein can be represented as follows:



Since specific proteins are needed by the human body, the proteins in food must be broken into their constituent amino acids, which are then used to construct new proteins in the body’s cells. The reaction in which a protein is broken down one amino acid at a time is shown in Fig. 12.19. Note that in this reaction a water molecule reacts with a protein molecule to produce an amino acid and a new protein containing one less amino acid. Without the enzymes found in human cells, this reaction would be much too slow to be useful. One of these enzymes is *carboxypeptidase-A*, a zinc-containing protein (Fig. 12.20).

Carboxypeptidase-A captures the protein to be acted on (called the *substrate*) in a special groove and positions the substrate so that the end is in the active site, where the catalysis occurs (Fig. 12.21). Note that the Zn^{2+} ion bonds to the oxygen of the $\text{C}=\text{O}$ (carbonyl) group. This polarizes the electron density in the carbonyl group, allowing the neigh-

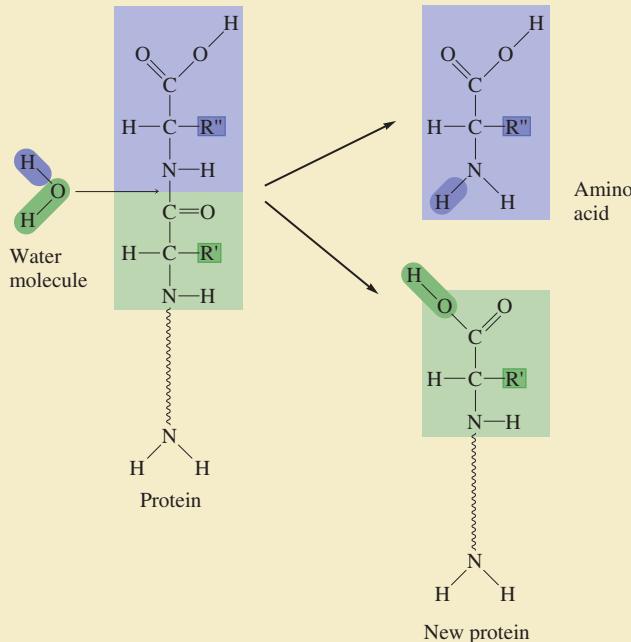
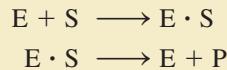


FIGURE 12.19

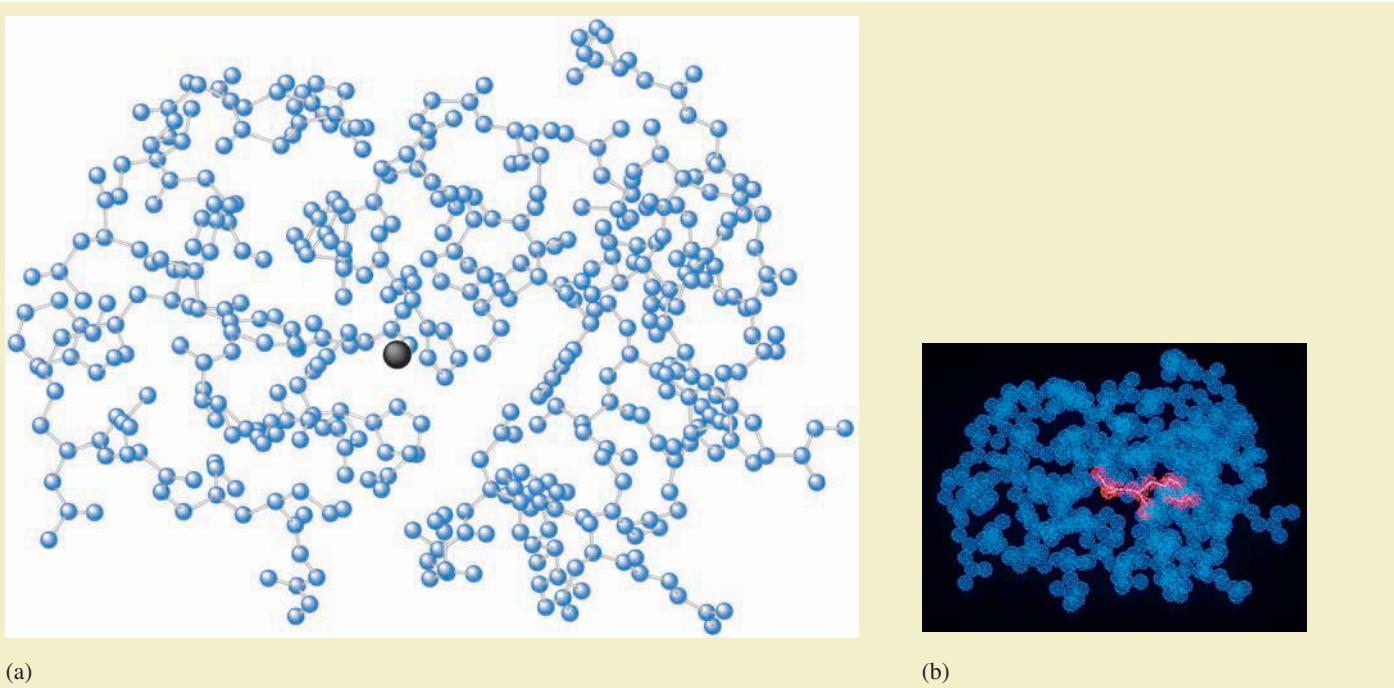
The removal of the end amino acid from a protein by reaction with a molecule of water. The products are an amino acid and a new, smaller protein.

boring C—N bond to be broken much more easily. When the reaction is completed, the remaining portion of the substrate protein and the newly formed amino acid are released by the enzyme.

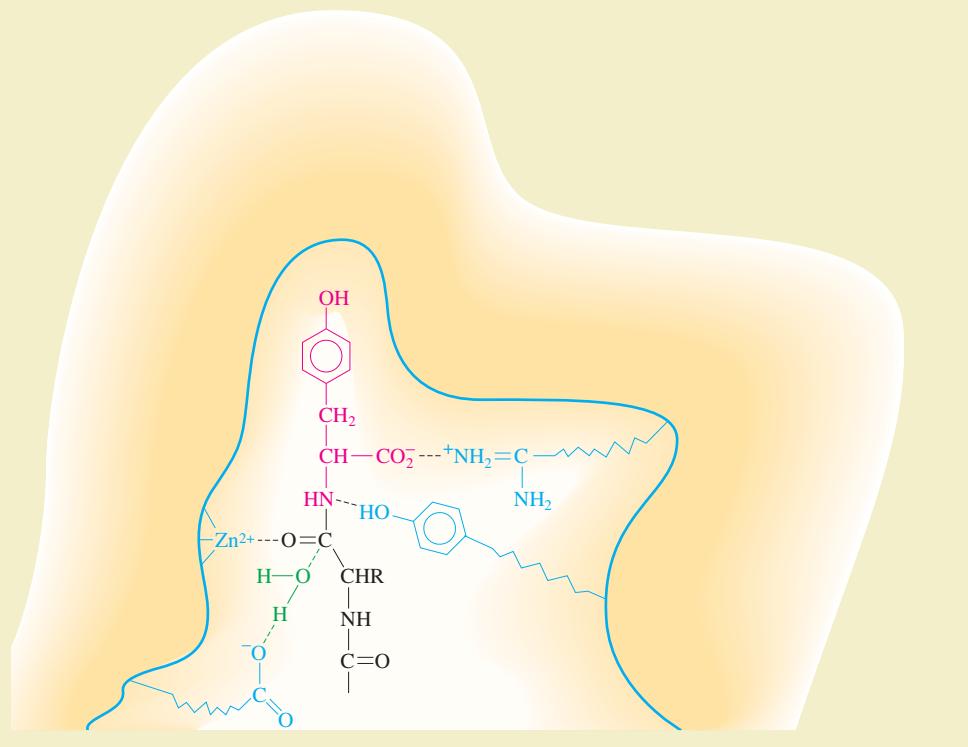
The process just described for carboxypeptidase-A is characteristic of the behavior of other enzymes. Enzyme catalysis can be represented by the series of reactions shown below:



where E represents the enzyme, S represents the substrate, $\text{E} \cdot \text{S}$ represents the enzyme–substrate complex, and P represents the products. The enzyme and substrate form a complex, where the reaction occurs. The enzyme then releases the product and is ready to repeat the process. The most amazing thing about enzymes is their efficiency. Because an enzyme plays its catalytic role over and over and very rapidly, only a tiny amount of enzyme is required. This makes the isolation of enzymes for study quite difficult.

**FIGURE 12.20**

(a) The structure of the enzyme carboxypeptidase-A, which contains 307 amino acids. The zinc ion is shown above as a black sphere in the center. (b) Carboxypeptidase-A with a substrate (pink) in place.



Key Terms

chemical kinetics

Section 12.1

reaction rate

instantaneous rate

Section 12.2

rate law

rate constant

order

(differential) rate law

integrated rate law

Section 12.3

method of initial rates

initial rate

overall reaction order

Section 12.4

first-order reaction

integrated first-order rate law

half-life of a reactant

integrated second-order rate law

zero-order reaction

integrated zero-order rate law

pseudo-first-order rate law

Section 12.6

reaction mechanism

intermediate

elementary step

molecularity

unimolecular step

bimolecular step

termolecular step

rate-determining step

Section 12.7

collision model

activation energy

activated complex (transition state)

molecular orientations

steric factor

Arrhenius equation

frequency factor

Section 12.8

enzyme

catalyst

homogeneous catalyst

heterogeneous catalyst

adsorption

For Review

Chemical kinetics

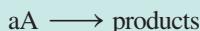
- The study of the factors that control the rate (speed) of a chemical reaction
 - Rate is defined in terms of the change in concentration of a given reaction component per unit time
 - Kinetic measurements are often made under conditions where the reverse reaction is insignificant
- The kinetic and thermodynamic properties of a reaction are not fundamentally related

Rate laws

- Differential rate law: describes the rate as a function of concentration

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^n$$

- k is the rate constant
- n is the order; not related to the coefficients in the balanced equation
- Integrated rate law: describes the concentration as a function of time
 - For a reaction of the type



for which

$$\text{Rate} = k[\text{A}]^n$$

$$n = 0: \quad [\text{A}] = -kt + [\text{A}]_0$$

$$t_{1/2} = \frac{[\text{A}]_0}{2k}$$

$$n = 1: \quad \ln[\text{A}] = -kt + \ln[\text{A}]_0$$

$$t_{1/2} = \frac{0.693}{k}$$

$$n = 2: \quad \frac{1}{[\text{A}]} = kt + \frac{1}{[\text{A}]_0}$$

$$t_{1/2} = \frac{1}{k[\text{A}]_0}$$

- The value of k can be determined from the plot of the appropriate function of $[\text{A}]$ versus t

Reaction mechanism

- Series of elementary steps by which an overall reaction occurs
 - Elementary step: rate law for the step can be written from the molecularity of the reaction
- Two requirements for an acceptable mechanism:
 - The elementary steps sum to give the correct overall balanced equation
 - The mechanism agrees with the experimentally determined rate law
- Simple reactions can have an elementary step that is slower than all of the other steps; which is called the rate-determining step.

Kinetic models

- The simplest model to account for reaction kinetics is the collision model
 - Molecules must collide to react
 - The collision kinetic energy furnishes the potential energy needed to enable the reactants to rearrange to form products

- A certain threshold energy called the activation energy (E_a) is necessary for a reaction to occur
- The relative orientations of the colliding reactants are also a determining factor in the reaction rate
- This model leads to the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

- A depends on the collision frequency and relative orientation of the molecules
- The value of E_a can be found by obtaining the values of k at several temperatures

Catalyst

- Speeds up a reaction without being consumed
- Works by providing a lower-energy pathway for the reaction
- Enzymes are biological catalysts
- Catalysts can be classified as homogeneous or heterogeneous
 - Homogeneous: exist in the same phase as the reactants
 - Heterogeneous: exist in a different phase than the reactants

REVIEW QUESTIONS

1. Define *reaction rate*. Distinguish between the initial rate, average rate, and instantaneous rate of a chemical reaction. Which of these rates is usually fastest? The initial rate is the rate used by convention. Give a possible explanation as to why.
2. Distinguish between the differential rate law and the integrated rate law. Which of these is often called just the “rate law”? What is k in a rate law, and what are orders in a rate law? Explain.
3. One experimental procedure that can be used to determine the rate law of a reaction is the method of initial rates. What data are gathered in the method of initial rates, and how are these data manipulated to determine k and the orders of the species in the rate law? Are the units for k , the rate constant, the same for all rate laws? Explain. If a reaction is first order in A, what happens to the rate if [A] is tripled? If the initial rate for a reaction increases by a factor of 16 when [A] is quadrupled, what is the order of n ? If a reaction is third order in A and [A] is doubled, what happens to the initial rate? If a reaction is zero order, what effect does [A] have on the initial rate of a reaction?
4. The initial rate for a reaction is equal to the slope of the tangent line at $t \approx 0$ in a plot of [A] versus time. From calculus, initial rate = $\frac{-d[A]}{dt}$. Therefore, the differential rate law for a reaction is Rate = $\frac{-d[A]}{dt} = k[A]^n$. Assuming you have some calculus in your background, derive the zero-, first-, and second-order integrated rate laws using the differential rate law.
5. Consider the zero-, first-, and second-order integrated rate laws. If you have concentration versus time data for some species in a reaction, what plots would you make to “prove” a reaction is either zero, first, or second order? How would the rate constant, k , be determined from such a plot? What does the y-intercept equal in each plot? When a rate law contains the concentration of two or more species, how can plots be used to determine k and the orders of the species in the rate law?
6. Derive expressions for the half-life of zero-, first-, and second-order reactions using the integrated rate law for each order. How does each half-life depend on

concentration? If the half-life for a reaction is 20. seconds, what would be the second half-life assuming the reaction is either zero, first, or second order?

7. Define each of the following.

- elementary step
- molecularity
- reaction mechanism
- intermediate
- rate-determining step

What two requirements must be met to call a mechanism plausible? Why say a “plausible” mechanism instead of the “correct” mechanism? Is it true that most reactions occur by a one-step mechanism? Explain.

8. What is the premise underlying the collision model? How is the rate affected by each of the following?

- activation energy
- temperature
- frequency of collisions
- orientation of collisions

Sketch a potential energy versus reaction progress plot for an endothermic reaction and for an exothermic reaction. Show ΔE and E_a in both plots. When concentrations and temperatures are equal, would you expect the rate of the forward reaction to be equal to, greater than, or less than the rate of the reverse reaction if the reaction is exothermic? Endothermic?

9. Give the Arrhenius equation. Take the natural log of both sides and place this equation in the form of a straight-line equation ($y = mx + b$). What data would you need and how would you graph those data to get a linear relationship using the Arrhenius equation? What does the slope of the straight line equal? What does the y-intercept equal? What are the units of R in the Arrhenius equation? Explain how if you know the rate constant value at two different temperatures, you can determine the activation energy for the reaction.

10. Why does a catalyst increase the rate of a reaction? What is the difference between a homogeneous catalyst and a heterogeneous catalyst? Would a given reaction necessarily have the same rate law for both a catalyzed and an uncatalyzed pathway? Explain.

Active Learning Questions*

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

- Define *stability* from both a kinetic and thermodynamic perspective. Give examples to show the differences in these concepts.
- Describe at least two experiments you could perform to determine a rate law.
- Make a graph of $[A]$ versus time for zero-, first-, and second-order reactions. From these graphs, compare successive half-lives.

*In the Questions and the Exercises, the term *rate law* always refers to the differential rate law.

4. How does temperature affect k , the rate constant? Explain.

5. Consider the following statements: “In general, the rate of a chemical reaction increases a bit at first because it takes a while for the reaction to get ‘warmed up.’ After that, however, the rate of the reaction decreases because its rate is dependent on the concentrations of the reactants, and these are decreasing.” Indicate everything that is correct in these statements, and indicate everything that is incorrect. Correct the incorrect statements and explain.

6. For the reaction $A + B \rightarrow C$, explain at least two ways in which the rate law could be zero order in chemical A.

7. A friend of yours states, “A balanced equation tells us how chemicals interact. Therefore, we can determine the rate law directly from the balanced equation.” What do you tell your friend?

8. Provide a conceptual rationale for the differences in the half-lives of zero-, first-, and second-order reactions.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

9. Define what is meant by unimolecular and bimolecular steps. Why are termolecular steps infrequently seen in chemical reactions?
10. Hydrogen reacts explosively with oxygen. However, a mixture of H₂ and O₂ can exist indefinitely at room temperature. Explain why H₂ and O₂ do not react under these conditions.
11. For the reaction



the observed rate law is

$$\text{Rate} = k[\text{NO}]^2[\text{H}_2]$$

Which of the changes listed below would affect the value of the rate constant *k*?

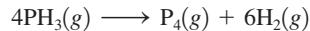
- a. increasing the partial pressure of hydrogen gas
 - b. changing the temperature
 - c. using an appropriate catalyst
12. The rate law for a reaction can be determined only from experiment and not from the balanced equation. Two experimental procedures were outlined in Chapter 12. What are these two procedures? Explain how each method is used to determine rate laws.
 13. Table 12.2 illustrates how the average rate of a reaction decreases with time. Why does the average rate decrease with time? How does the instantaneous rate of a reaction depend on time? Why are initial rates used by convention?
 14. The type of rate law for a reaction, either the differential rate law or the integrated rate, is usually determined by which data is easiest to collect. Explain.
 15. The initial rate of a reaction doubles as the concentration of one of the reactants is quadrupled. What is the order of this reactant? If a reactant has a -1 order, what happens to the initial rate when the concentration of that reactant increases by a factor of two?
 16. Reactions that require a metal catalyst are often zero order after a certain amount of reactant(s) are present. Explain.
 17. The central idea of the collision model is that molecules must collide in order to react. Give two reasons why not all collisions of reactant molecules result in product formation.
 18. Would the slope of a ln *k* versus 1/T (K) plot for a catalyzed reaction be more or less negative than the slope of the ln *k* versus 1/T (K) plot for the uncatalyzed reaction? Explain.

Exercises

In this section similar exercises are paired.

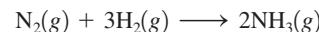
Reaction Rates

19. Consider the reaction



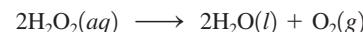
If, in a certain experiment, over a specific time period, 0.0048 mol PH₃ is consumed in a 2.0-L container each second of reaction, what are the rates of production of P₄ and H₂ in this experiment?

20. In the Haber process for the production of ammonia,



what is the relationship between the rate of production of ammonia and the rate of consumption of hydrogen?

21. At 40°C, H₂O₂(*aq*) will decompose according to the following reaction:



The following data were collected for the concentration of H₂O₂ at various times.

Time (s)	[H ₂ O ₂] (mol/L)
0	1.000
2.16 × 10 ⁴	0.500
4.32 × 10 ⁴	0.250

- a. Calculate the average rate of decomposition of H₂O₂ between 0 and 2.16 × 10⁴ s. Use this rate to calculate the average rate of production of O₂(g) over the same time period.
- b. What are these rates for the time period 2.16 × 10⁴ s to 4.32 × 10⁴ s?

22. Consider the general reaction



and the following average rate data over some time period Δ*t*:

$$-\frac{\Delta \text{A}}{\Delta t} = 0.0080 \text{ mol/L} \cdot \text{s}$$

$$-\frac{\Delta \text{B}}{\Delta t} = 0.0120 \text{ mol/L} \cdot \text{s}$$

$$\frac{\Delta \text{C}}{\Delta t} = 0.0160 \text{ mol/L} \cdot \text{s}$$

Determine a set of possible coefficients to balance this general reaction.

23. What are the units for each of the following if the concentrations are expressed in moles per liter and the time in seconds?
 - a. rate of a chemical reaction
 - b. rate constant for a zero-order rate law
 - c. rate constant for a first-order rate law
 - d. rate constant for a second-order rate law
 - e. rate constant for a third-order rate law

24. The rate law for the reaction



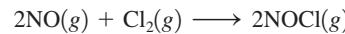
is

$$\text{Rate} = k[\text{Cl}_2]^{1/2}[\text{CHCl}_3]$$

What are the units for *k*, assuming time in seconds and concentration in mol/L?

Rate Laws from Experimental Data: Initial Rates Method

25. The reaction



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was studied at -10°C . The following results were obtained where

$$\text{Rate} = -\frac{\Delta[\text{Cl}_2]}{\Delta t}$$

[NO] ₀ (mol/L)	[Cl ₂] ₀ (mol/L)	Initial Rate (mol/L · min)
0.10	0.10	0.18
0.10	0.20	0.36
0.20	0.20	1.45

- What is the rate law?
- What is the value of the rate constant?

26. The reaction



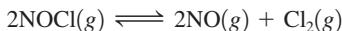
was studied at 25°C . The following results were obtained where

$$\text{Rate} = -\frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t}$$

[I ⁻] ₀ (mol/L)	[S ₂ O ₈ ²⁻] ₀ (mol/L)	Initial Rate (mol/L · s)
0.080	0.040	12.5×10^{-6}
0.040	0.040	6.25×10^{-6}
0.080	0.020	6.25×10^{-6}
0.032	0.040	5.00×10^{-6}
0.060	0.030	7.00×10^{-6}

- Determine the rate law.
- Calculate a value for the rate constant for each experiment and an average value for the rate constant.

27. The decomposition of nitrosyl chloride was studied:



The following data were obtained where

$$\text{Rate} = -\frac{\Delta[\text{NOCl}]}{\Delta t}$$

[NOCl] ₀ (molecules/cm ³)	Initial Rate (molecules/cm ³ · s)
3.0×10^{16}	5.98×10^4
2.0×10^{16}	2.66×10^4
1.0×10^{16}	6.64×10^3
4.0×10^{16}	1.06×10^5

- What is the rate law?
- Calculate the rate constant.

- Calculate the rate constant when concentrations are given in moles per liter.

28. The following data were obtained for the gas-phase decomposition of dinitrogen pentoxide,



[N ₂ O ₅] ₀ (mol/L)	Initial Rate (mol/L · s)
0.0750	8.90×10^{-4}
0.190	2.26×10^{-3}
0.275	3.26×10^{-3}
0.410	4.85×10^{-3}

Defining the rate as $-\Delta[\text{N}_2\text{O}_5]/\Delta t$, write the rate law and calculate the value of the rate constant.

29. The rate of the reaction between hemoglobin (Hb) and carbon monoxide (CO) was studied at 20°C . The following data were collected with all concentration units in $\mu\text{mol/L}$. (A hemoglobin concentration of $2.21 \mu\text{mol/L}$ is equal to $2.21 \times 10^{-6} \text{ mol/L}$.)

[Hb] ₀ ($\mu\text{mol/L}$)	[CO] ₀ ($\mu\text{mol/L}$)	Initial Rate ($\mu\text{mol/L} \cdot \text{s}$)
2.21	1.00	0.619
4.42	1.00	1.24
4.42	3.00	3.71

- Determine the orders of this reaction with respect to Hb and CO.
- Determine the rate law.
- Calculate the value of the rate constant.
- What would be the initial rate for an experiment with $[\text{Hb}]_0 = 3.36 \mu\text{mol/L}$ and $[\text{CO}]_0 = 2.40 \mu\text{mol/L}$?

30. The following data were obtained for the reaction



$$\text{where} \quad \text{Rate} = -\frac{\Delta[\text{ClO}_2]}{\Delta t}$$

[ClO ₂] ₀ (mol/L)	[OH ⁻] ₀ (mol/L)	Initial Rate (mol/L · s)
0.0500	0.100	5.75×10^{-2}
0.100	0.100	2.30×10^{-1}
0.100	0.0500	1.15×10^{-1}

- Determine the rate law and the value of the rate constant.
- What would be the initial rate for an experiment with $[\text{ClO}_2]_0 = 0.175 \text{ mol/L}$ and $[\text{OH}^-]_0 = 0.0844 \text{ mol/L}$?

Integrated Rate Laws

- 31.** The decomposition of hydrogen peroxide was studied, and the following data were obtained at a particular temperature:

Time (s)	[H ₂ O ₂] (mol/L)
0	1.00
120 ± 1	0.91
300 ± 1	0.78
600 ± 1	0.59
1200 ± 1	0.37
1800 ± 1	0.22
2400 ± 1	0.13
3000 ± 1	0.082
3600 ± 1	0.050

Assuming that

$$\text{Rate} = -\frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t}$$

determine the rate law, the integrated rate law, and the value of the rate constant. Calculate [H₂O₂] at 4000. s after the start of the reaction.

- 32.** A certain reaction has the following general form:



At a particular temperature and [A]₀ = 2.00 × 10⁻² M, concentration versus time data were collected for this reaction, and a plot of ln[A] versus time resulted in a straight line with a slope value of $-2.97 \times 10^{-2} \text{ min}^{-1}$.

- a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
- b. Calculate the half-life for this reaction.
- c. How much time is required for the concentration of A to decrease to 2.50×10^{-3} M?

- 33.** The rate of the reaction



depends only on the concentration of nitrogen dioxide below 225°C. At a temperature below 225°C, the following data were collected:

Time (s)	[NO ₂] (mol/L)
0	0.500
1.20×10^3	0.444
3.00×10^3	0.381
4.50×10^3	0.340
9.00×10^3	0.250
1.80×10^4	0.174

Determine the rate law, the integrated law, and the value of the rate constant. Calculate [NO₂] at 2.70×10^4 s after the start of the reaction.

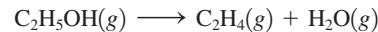
- 34.** A certain reaction has the following general form:



At a particular temperature and [A]₀ = 2.80×10^{-3} M, concentration versus time data were collected for this reaction, and a plot of 1/[A] versus time resulted in a straight line with a slope value of $+3.60 \times 10^{-2}$ L/mol · s.

- a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
- b. Calculate the half-life for this reaction.
- c. How much time is required for the concentration of A to decrease to 7.00×10^{-4} M?

- 35.** The decomposition of ethanol (C₂H₅OH) on an alumina (Al₂O₃) surface



was studied at 600 K. Concentration versus time data were collected for this reaction, and a plot of [A] versus time resulted in a straight line with a slope of -4.00×10^{-5} mol/L · s.

- a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
- b. If the initial concentration of C₂H₅OH was 1.25×10^{-2} M, calculate the half-life for this reaction.
- c. How much time is required for all the 1.25×10^{-2} M C₂H₅OH to decompose?

- 36.** At 500 K in the presence of a copper surface, ethanol decomposes according to the equation



The pressure of C₂H₅OH was measured as a function of time and the following data were obtained:

Time (s)	P _{C₂H₅OH} (torr)
0	250.
100.	237
200.	224
300.	211
400.	198
500.	185

Since the pressure of a gas is directly proportional to the concentration of gas, we can express the rate law for a gaseous reaction in terms of partial pressures. Using the above data, deduce the rate law, the integrated rate law, and the value of the rate constant, all in terms of pressure units in atm and time in seconds. Predict the pressure of C₂H₅OH after 900. s from the start of the reaction. (Hint: To determine the order of the reaction with respect to C₂H₅OH, compare how the pressure of C₂H₅OH decreases with each time listing.)

Chapter Twelve Chemical Kinetics

37. The dimerization of butadiene



was studied at 500. K, and the following data were obtained:

Time (s)	[C ₄ H ₆] (mol/L)
195	1.6 × 10 ⁻²
604	1.5 × 10 ⁻²
1246	1.3 × 10 ⁻²
2180	1.1 × 10 ⁻²
6210	0.68 × 10 ⁻²

Assuming that

$$\text{Rate} = -\frac{\Delta[\text{C}_4\text{H}_6]}{\Delta t}$$

determine the form of the rate law, the integrated rate law, and the rate constant for this reaction. (These are actual experimental data, so they may not give a perfectly straight line.)

38. The rate of the reaction



was studied at a certain temperature.

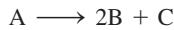
- a. In the first set of experiments, NO₂ was in large excess, at a concentration of 1.0×10^{13} molecules/cm³ with the following data collected:

Time (s)	[O] (atoms/cm ³)
0	5.0×10^9
1.0×10^{-2}	1.9×10^9
2.0×10^{-2}	6.8×10^8
3.0×10^{-2}	2.5×10^8

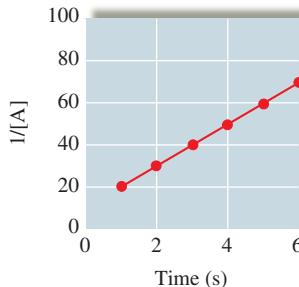
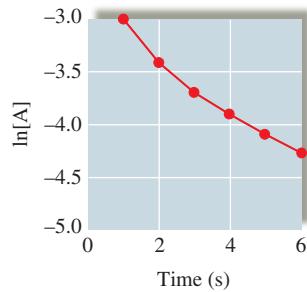
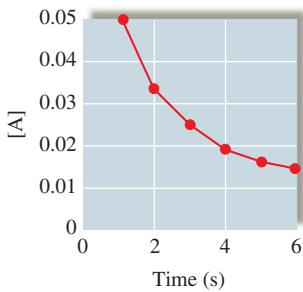
What is the order of the reaction with respect to oxygen atoms?

- b. The reaction is known to be first order with respect to NO₂. Determine the overall rate law and the value of the rate constant.

39. Experimental data for the reaction



have been plotted in the following three different ways (with concentration units in mol/L):

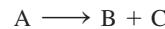


What is the order of the reaction with respect to A and what is the initial concentration of A?

- 40.** Consider the data plotted in Exercise 39 when answering the following questions.

- a. What is the concentration of A after 9 s?
b. What are the first three half-lives for this experiment?

41. The reaction



is known to be zero order in A and to have a rate constant of 5.0×10^{-2} mol/L · s at 25°C. An experiment was run at 25°C where $[\text{A}]_0 = 1.0 \times 10^{-3}$ M.

- a. Write the integrated rate law for this reaction.
b. Calculate the half-life for the reaction.
c. Calculate the concentration of B after 5.0×10^{-3} s has elapsed.

- 42.** The radioactive isotope ³²P decays by first-order kinetics and has a half-life of 14.3 days. How long does it take for 95.0% of a sample of ³²P to decay?

- 43.** A first-order reaction is 75.0% complete in 320. s.
a. What are the first and second half-lives for this reaction?
b. How long does it take for 90.0% completion?

- 44.** The rate law for the decomposition of phosphine (PH₃) is

$$\text{Rate} = -\frac{\Delta[\text{PH}_3]}{\Delta t} = k[\text{PH}_3]$$

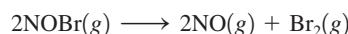
It takes 120. s for 1.00 M PH₃ to decrease to 0.250 M. How much time is required for 2.00 M PH₃ to decrease to a concentration of 0.350 M?

- 45.** Consider the following initial rate data for the decomposition of compound AB to give A and B:

[AB] ₀ (mol/L)	Initial Rate (mol/L · s)
0.200	3.20×10^{-3}
0.400	1.28×10^{-2}
0.600	2.88×10^{-2}

Determine the half-life for the decomposition reaction initially having 1.00 M AB present.

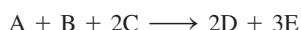
- 46.** The rate law for the reaction



at some temperature is

$$\text{Rate} = -\frac{\Delta[\text{NOBr}]}{\Delta t} = k[\text{NOBr}]^2$$

- If the half-life for this reaction is 2.00 s when $[\text{NOBr}]_0 = 0.900 \text{ M}$, calculate the value of k for this reaction.
 - How much time is required for the concentration of NOBr to decrease to 0.100 M ?
- 47.** For the reaction $\text{A} \rightarrow \text{products}$, successive half-lives are observed to be 10.0, 20.0, and 40.0 min for an experiment in which $[\text{A}]_0 = 0.10 \text{ M}$. Calculate the concentration of A at the following times.
- 80.0 min
 - 30.0 min
- 48.** Consider the hypothetical reaction



where the rate law is

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}][\text{B}]^2$$

An experiment is carried out where $[\text{A}]_0 = 1.0 \times 10^{-2} \text{ M}$, $[\text{B}]_0 = 3.0 \text{ M}$, and $[\text{C}]_0 = 2.0 \text{ M}$. The reaction is started, and after 8.0 seconds, the concentration of A is $3.8 \times 10^{-3} \text{ M}$.

- Calculate k for this reaction.
- Calculate the half-life for this experiment.
- Calculate the concentration of A after 13.0 seconds.
- Calculate the concentration of C after 13.0 seconds.

Reaction Mechanisms

- 49.** Write the rate laws for the following elementary reactions.

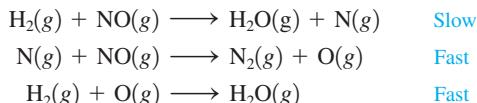
- $\text{CH}_3\text{NC}(g) \rightarrow \text{CH}_3\text{CN}(g)$
- $\text{O}_3(g) + \text{NO}(g) \rightarrow \text{O}_2(g) + \text{NO}_2(g)$
- $\text{O}_3(g) \rightarrow \text{O}_2(g) + \text{O}(g)$
- $\text{O}_3(g) + \text{O}(g) \rightarrow 2\text{O}_2(g)$

- 50.** The mechanisms shown below have been proposed to explain the kinetics of the reaction considered in Question 11. Which of the following are acceptable mechanisms? Explain.

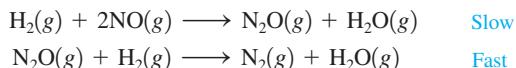
Mechanism I:



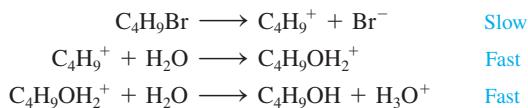
Mechanism II:



Mechanism III:

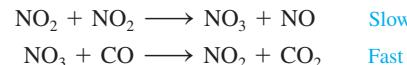


- 51.** A proposed mechanism for a reaction is



Write the rate law expected for this mechanism. What is the overall balanced equation for the reaction? What are the intermediates in the proposed mechanism?

- 52.** The mechanism for the reaction of nitrogen dioxide with carbon monoxide to form nitric oxide and carbon dioxide is thought to be

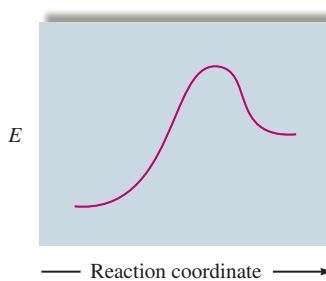


Write the rate law expected for this mechanism. What is the overall balanced equation for the reaction?

Temperature Dependence of Rate Constants and the Collision Model

- 53.** For the following reaction profile, indicate

- the positions of reactants and products.
- the activation energy.
- ΔE for the reaction.



- 54.** Draw a rough sketch of the energy profile for each of the following cases:

- $\Delta E = +10 \text{ kJ/mol}$, $E_a = 25 \text{ kJ/mol}$
- $\Delta E = -10 \text{ kJ/mol}$, $E_a = 50 \text{ kJ/mol}$
- $\Delta E = -50 \text{ kJ/mol}$, $E_a = 50 \text{ kJ/mol}$

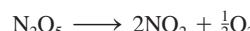
- 55.** The activation energy for the reaction



is 125 kJ/mol, and ΔE for the reaction is -216 kJ/mol . What is the activation energy for the reverse reaction $[\text{NO}(g) + \text{CO}_2(g) \longrightarrow \text{NO}_2(g) + \text{CO}(g)]$?

- 56.** For a certain process, the activation energy is greater for the forward reaction than for the reverse reaction. Does this reaction have a positive or negative value for ΔE ?

- 57.** The rate constant for the gas-phase decomposition of N_2O_5 ,



has the following temperature dependence:

$T \text{ (K)}$	$k \text{ (s}^{-1}\text{)}$
338	4.9×10^{-3}
318	5.0×10^{-4}
298	3.5×10^{-5}

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Make the appropriate graph using these data, and determine the activation energy for this reaction.

58. The reaction



in a certain solvent is first order with respect to $(CH_3)_3CBr$ and zero order with respect to OH^- . In several experiments, the rate constant k was determined at different temperatures. A plot of $\ln(k)$ versus $1/T$ was constructed resulting in a straight line with a slope value of -1.10×10^4 K and y -intercept of 33.5. Assume k has units of s^{-1} .

- a. Determine the activation energy for this reaction.
- b. Determine the value of the frequency factor A .
- c. Calculate the value of k at 25°C.

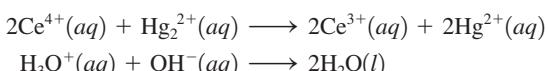
59. The activation energy for the decomposition of $HI(g)$ to $H_2(g)$ and $I_2(g)$ is 186 kJ/mol. The rate constant at 555 K is 3.52×10^{-7} L/mol · s. What is the rate constant at 645 K?

60. A first-order reaction has rate constants of 4.6×10^{-2} s $^{-1}$ and 8.1×10^{-2} s $^{-1}$ at 0°C and 20.0°C, respectively. What is the value of the activation energy?

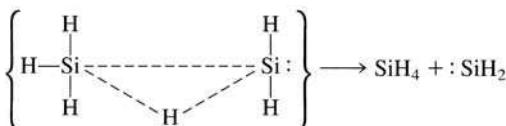
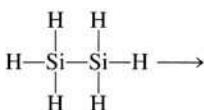
61. A certain reaction has an activation energy of 54.0 kJ/mol. As the temperature is increased from 22°C to a higher temperature, the rate constant increases by a factor of 7.00. Calculate the higher temperature.

62. Chemists commonly use a rule of thumb that an increase of 10 K in temperature doubles the rate of a reaction. What must the activation energy be for this statement to be true for a temperature increase from 25 to 35°C?

63. Which of the following reactions would you expect to proceed at a faster rate at room temperature? Why? (Hint: Think about which reaction would have the lower activation energy.)



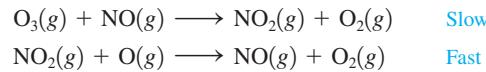
64. One reason suggested for the instability of long chains of silicon atoms is that the decomposition involves the transition state shown below:



The activation energy for such a process is 210 kJ/mol, which is less than either the Si—Si or the Si—H bond energy. Why would a similar mechanism not be expected to play a very important role in the decomposition of long chains of carbon atoms as seen in organic compounds?

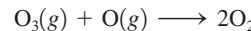
Catalysts

65. One mechanism for the destruction of ozone in the upper atmosphere is



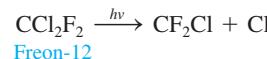
Overall reaction $O_3(g) + O(g) \longrightarrow 2O_2(g)$

- a. Which species is a catalyst?
- b. Which species is an intermediate?
- c. E_a for the uncatalyzed reaction



is 14.0 kJ. E_a for the same reaction when catalyzed is 11.9 kJ. What is the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25°C? Assume that the frequency factor A is the same for each reaction.

66. One of the concerns about the use of Freons is that they will migrate to the upper atmosphere, where chlorine atoms can be generated by the following reaction:



Chlorine atoms can act as a catalyst for the destruction of ozone. The activation energy for the reaction



is 2.1 kJ/mol. Which is the more effective catalyst for the destruction of ozone, Cl or NO? (See Exercise 65.)

67. Assuming that the mechanism for the hydrogenation of C_2H_4 given in Section 12.8 is correct, would you predict that the product of the reaction of C_2H_4 with D_2 would be CH_2D-CH_2D or CHD_2-CH_3 ? How could the reaction of C_2H_4 with D_2 be used to confirm the mechanism for the hydrogenation of C_2H_4 given in Section 12.8?

68. The decomposition of NH_3 to N_2 and H_2 was studied on two surfaces:

Surface	E_a (kJ/mol)
W	163
Os	197

Without a catalyst, the activation energy is 335 kJ/mol.

- a. Which surface is the better heterogeneous catalyst for the decomposition of NH_3 ? Why?
- b. How many times faster is the reaction at 298 K on the W surface compared with the reaction with no catalyst present? Assume that the frequency factor A is the same for each reaction.
- c. The decomposition reaction on the two surfaces obeys a rate law of the form

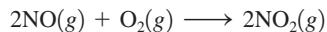
$$\text{Rate} = k \frac{[NH_3]}{[H_2]}$$

How can you explain the inverse dependence of the rate on the H₂ concentration?

- 69.** A famous chemical demonstration is the “magic genie” procedure, in which hydrogen peroxide decomposes to water and oxygen gas with the aid of a catalyst. The activation energy of this (uncatalyzed) reaction is 70.0 kJ/mol. When the catalyst is added, the activation energy (at 20.°C) is 42.0 kJ/mol. Theoretically, to what temperature (°C) would one have to heat the hydrogen peroxide solution so that the rate of the uncatalyzed reaction is equal to the rate of the catalyzed reaction at 20.°C? Assume the frequency factor *A* is constant and assume the initial concentrations are the same.
- 70.** The activation energy for a reaction is changed from 184 kJ/mol to 59.0 kJ/mol at 600. K by the introduction of a catalyst. If the uncatalyzed reaction takes about 2400 years to occur, about how long will the catalyzed reaction take? Assume the frequency factor *A* is constant and assume the initial concentrations are the same.

Additional Exercises

- 71.** The reaction



was studied, and the following data were obtained where

$$\text{Rate} = -\frac{\Delta[\text{O}_2]}{\Delta t}$$

[NO] ₀ (molecules/cm ³)	[O ₂] ₀ (molecules/cm ³)	Initial Rate (molecules/cm ³ · s)
1.00 × 10 ¹⁸	1.00 × 10 ¹⁸	2.00 × 10 ¹⁶
3.00 × 10 ¹⁸	1.00 × 10 ¹⁸	1.80 × 10 ¹⁷
2.50 × 10 ¹⁸	2.50 × 10 ¹⁸	3.13 × 10 ¹⁷

What would be the initial rate for an experiment where [NO]₀ = 6.21 × 10¹⁸ molecules/cm³ and [O₂]₀ = 7.36 × 10¹⁸ molecules/cm³?

- 72.** Sulfuryl chloride (SO₂Cl₂) decomposes to sulfur dioxide (SO₂) and chlorine (Cl₂) by reaction in the gas phase. The following pressure data were obtained when a sample containing 5.00 × 10⁻² mol sulfuryl chloride was heated to 600. K in a 5.00 × 10⁻¹-L container.

Time (hours):	0.00	1.00	2.00	4.00	8.00	16.00
P _{SO₂Cl₂} (atm):	4.93	4.26	3.52	2.53	1.30	0.34

Defining the rate as $-\frac{\Delta[\text{SO}_2\text{Cl}_2]}{\Delta t}$,

- a. determine the value of the rate constant for the decomposition of sulfuryl chloride at 600. K.
 b. what is the half-life of the reaction?
 c. what fraction of the sulfuryl chloride remains after 20.0 h?

- 73.** For the reaction



the following data were collected, where

$$\text{Rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

Time (s)	T = 338 K [N ₂ O ₅]	T = 318 K [N ₂ O ₅]
0	1.00 × 10 ⁻¹ M	1.00 × 10 ⁻¹ M
100.	6.14 × 10 ⁻² M	9.54 × 10 ⁻² M
300.	2.33 × 10 ⁻² M	8.63 × 10 ⁻² M
600.	5.41 × 10 ⁻³ M	7.43 × 10 ⁻² M
900.	1.26 × 10 ⁻³ M	6.39 × 10 ⁻² M

Calculate E_a for this reaction.

- 74.** Experimental values for the temperature dependence of the rate constant for the gas-phase reaction

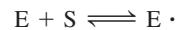


are as follows:

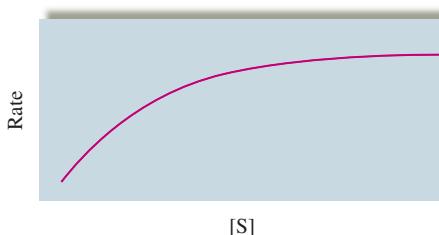
T (K)	k (L/mol · s)
195	1.08 × 10 ⁹
230.	2.95 × 10 ⁹
260.	5.42 × 10 ⁹
298	12.0 × 10 ⁹
369	35.5 × 10 ⁹

Make the appropriate graph using these data, and determine the activation energy for this reaction.

- 75.** For enzyme-catalyzed reactions that follow the mechanism



a graph of the rate as a function of [S], the concentration of the substrate, has the following appearance:



Note that at higher substrate concentrations the rate no longer changes with [S]. Suggest a reason for this.

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- 76.** The activation energy of a certain uncatalyzed biochemical reaction is 50.0 kJ/mol. In the presence of a catalyst at 37°C, the rate constant for the reaction increases by a factor of 2.50×10^3 as compared with the uncatalyzed reaction. Assuming the frequency factor A is the same for both the catalyzed and uncatalyzed reactions, calculate the activation energy for the catalyzed reaction.

- 77.** Consider the reaction



where the rate law is defined as

$$-\frac{\Delta[A]}{\Delta t} = k[A]^2[B][C]$$

An experiment is carried out where $[B]_0 = [C]_0 = 1.00 M$ and $[A]_0 = 1.00 \times 10^{-4} M$.

- a. If after 3.00 min, $[A] = 3.26 \times 10^{-5} M$, calculate the value of k .
- b. Calculate the half-life for this experiment.
- c. Calculate the concentration of B and the concentration of A after 10.0 min.

Challenge Problems

- 78.** Consider a reaction of the type $aA \rightarrow \text{products}$, in which the rate law is found to be $\text{rate} = k[A]^3$ (termolecular reactions are improbable but possible). If the first half-life of the reaction is found to be 40. s, what is the time for the second half-life? Hint: Using your calculus knowledge, derive the integrated rate law from the differential rate law for a termolecular reaction:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^3$$

- 79.** A study was made of the effect of the hydroxide concentration on the rate of the reaction

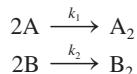


The following data were obtained:

$[I^-]_0$ (mol/L)	$[OCl^-]_0$ (mol/L)	$[OH^-]_0$ (mol/L)	Initial Rate (mol/L · s)
0.0013	0.012	0.10	9.4×10^{-3}
0.0026	0.012	0.10	18.7×10^{-3}
0.0013	0.0060	0.10	4.7×10^{-3}
0.0013	0.018	0.10	14.0×10^{-3}
0.0013	0.012	0.050	18.7×10^{-3}
0.0013	0.012	0.20	4.7×10^{-3}
0.0013	0.018	0.20	7.0×10^{-3}

Determine the rate law and the value of the rate constant for this reaction.

- 80.** Two isomers (A and B) of a given compound dimerize as follows:



Both processes are known to be second order in reactant, and k_1 is known to be 0.250 L/mol · s at 25°C. In a particular experiment A and B were placed in separate containers at 25°C, where $[A]_0 = 1.00 \times 10^{-2} M$ and $[B]_0 = 2.50 \times 10^{-2} M$. It was found that after each reaction had progressed for 3.00 min, $[A] = 3.00[B]$. In this case the rate laws are defined as

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k_1[A]^2$$

$$\text{Rate} = -\frac{\Delta[B]}{\Delta t} = k_2[B]^2$$

- a. Calculate the concentration of A_2 after 3.00 min.
- b. Calculate the value of k_2 .
- c. Calculate the half-life for the experiment involving A.

- 81.** The reaction



was studied by performing two experiments. In the first experiment the rate of disappearance of NO was followed in the presence of a large excess of O_3 . The results were as follows ($[O_3]$ remains effectively constant at 1.0×10^{14} molecules/cm³):

Time (ms)	[NO] (molecules/cm ³)
0	6.0×10^8
100 ± 1	5.0×10^8
500 ± 1	2.4×10^8
700 ± 1	1.7×10^8
1000 ± 1	9.9×10^7

In the second experiment [NO] was held constant at 2.0×10^{14} molecules/cm³. The data for the disappearance of O_3 are as follows:

Time (ms)	[O ₃] (molecules/cm ³)
0	1.0×10^{10}
50 ± 1	8.4×10^9
100 ± 1	7.0×10^9
200 ± 1	4.9×10^9
300 ± 1	3.4×10^9

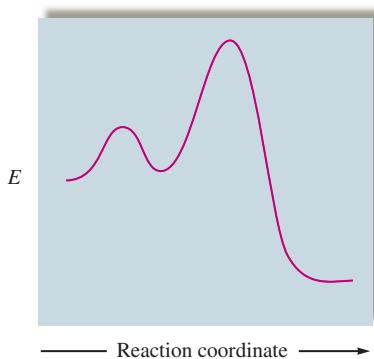
- a. What is the order with respect to each reactant?
- b. What is the overall rate law?
- c. What is the value of the rate constant from each set of experiments?

$$\text{Rate} = k'[NO]^x \quad \text{Rate} = k''[O_3]^y$$

- d. What is the value of the rate constant for the overall rate law?

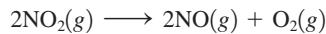
$$\text{Rate} = k[NO]^x[O_3]^y$$

- 82.** Most reactions occur by a series of steps. The energy profile for a certain reaction that proceeds by a two-step mechanism is



- On the energy profile, indicate
- The positions of reactants and products.
 - The activation energy for the overall reaction.
 - ΔE for the reaction.
 - Which point on the plot represents the energy of the intermediate in the two-step reaction?
 - Which step in the mechanism for this reaction is rate determining, the first or the second step? Explain.

- 83.** Experiments during a recent summer on a number of fireflies (small beetles, *Lampyridae photinus*) showed that the average interval between flashes of individual insects was 16.3 s at 21.0°C and 13.0 s at 27.8°C.
- What is the apparent activation energy of the reaction that controls the flashing?
 - What would be the average interval between flashes of an individual firefly at 30.0°C?
 - Compare the observed intervals and the one you calculated in part b to the rule of thumb that the Celsius temperature is 54 minus twice the interval between flashes.
- 84.** The decomposition of $\text{NO}_2(g)$ occurs by the following bimolecular elementary reaction:



The rate constant at 273 K is $2.3 \times 10^{-12} \text{ L/mol} \cdot \text{s}$, and the activation energy is 111 kJ/mol. How long will it take for the concentration of $\text{NO}_2(g)$ to decrease from an initial partial pressure of 2.5 atm to 1.5 atm at 500. K? Assume ideal gas behavior.

- 85.** The following data were collected in two studies of the reaction



Time (s)	Experiment 1		Experiment 2	
	[A] (mol/L) $\times 10^{-2}$			
0	10.0		10.0	
20.	6.67		5.00	
40.	5.00		3.33	
60.	4.00		2.50	
80.	3.33		2.00	
100.	2.86		1.67	
120.	2.50		1.43	

In experiment 1, $[\text{B}]_0 = 5.0 \text{ M}$.

In experiment 2, $[\text{B}]_0 = 10.0 \text{ M}$.

$$\text{Rate} = \frac{-\Delta[\text{A}]}{\Delta t}$$

- Why is [B] much greater than [A]?
- Give the rate law and value for k for this reaction.

- 86.** The following data were collected in two studies of the reaction



Time (s)	Experiment 1 [H ₂] (mol/L)	Experiment 2 [H ₂] (mol/L)
0.	1.0×10^{-2}	1.0×10^{-2}
10.	8.4×10^{-3}	5.0×10^{-3}
20.	7.1×10^{-3}	2.5×10^{-3}
30.	?	1.3×10^{-3}
40.	5.0×10^{-3}	6.3×10^{-4}

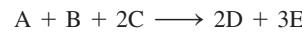
In experiment 1, $[\text{NO}]_0 = 10.0 \text{ M}$.

In experiment 2, $[\text{NO}]_0 = 20.0 \text{ M}$.

$$\text{Rate} = \frac{-\Delta[\text{H}_2]}{\Delta t}$$

- Use the concentration versus time data to determine the rate law for the reaction.
- Solve for the rate constant (k) for the reaction. Include units.
- Calculate the concentration of H₂ in experiment 1 at $t = 30$. s.

- 87.** Consider the hypothetical reaction



In a study of this reaction three experiments were run at the same temperature. The rate is defined as $-\Delta[\text{B}]/\Delta t$.

Experiment 1:

$$[\text{A}]_0 = 2.0 \text{ M} \quad [\text{B}]_0 = 1.0 \times 10^{-3} \text{ M} \quad [\text{C}]_0 = 1.0 \text{ M}$$

[B] (mol/L)	Time (s)
2.7×10^{-4}	1.0×10^5
1.6×10^{-4}	2.0×10^5
1.1×10^{-4}	3.0×10^5
8.5×10^{-5}	4.0×10^5
6.9×10^{-5}	5.0×10^5
5.8×10^{-5}	6.0×10^5

Experiment 2:

$$[\text{A}]_0 = 1.0 \times 10^{-2} \text{ M} \quad [\text{B}]_0 = 3.0 \text{ M} \quad [\text{C}]_0 = 1.0 \text{ M}$$

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[A] (mol/L)	Time (s)
8.9×10^{-3}	1.0
7.1×10^{-3}	3.0
5.5×10^{-3}	5.0
3.8×10^{-3}	8.0
2.9×10^{-3}	10.0
2.0×10^{-3}	13.0

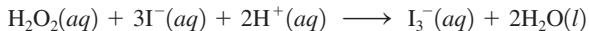
Experiment 3:

$$[A]_0 = 10.0 \text{ M} \quad [B]_0 = 5.0 \text{ M} \quad [C]_0 = 5.0 \times 10^{-1} \text{ M}$$

[C] (mol/L)	Time (s)
0.43	1.0×10^{-2}
0.36	2.0×10^{-2}
0.29	3.0×10^{-2}
0.22	4.0×10^{-2}
0.15	5.0×10^{-2}
0.08	6.0×10^{-2}

Write the rate law for this reaction, and calculate the rate constant.

88. Hydrogen peroxide and the iodide ion react in acidic solution as follows:



The kinetics of this reaction were studied by following the decay of the concentration of H_2O_2 and constructing plots of $\ln[\text{H}_2\text{O}_2]$ versus time. All the plots were linear and all solutions had $[\text{H}_2\text{O}_2]_0 = 8.0 \times 10^{-4} \text{ mol/L}$. The slopes of these straight lines depended on the initial concentrations of I^- and H^+ . The results follow:

$[\text{I}^-]_0$ (mol/L)	$[\text{H}^+]_0$ (mol/L)	Slope (min ⁻¹)
0.1000	0.0400	-0.120
0.3000	0.0400	-0.360
0.4000	0.0400	-0.480
0.0750	0.0200	-0.0760
0.0750	0.0800	-0.118
0.0750	0.1600	-0.174

The rate law for this reaction has the form

$$\text{Rate} = \frac{-\Delta[\text{H}_2\text{O}_2]}{\Delta t} = (k_1 + k_2[\text{H}^+])[\text{I}^-]^m[\text{H}_2\text{O}_2]^n$$

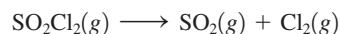
- a. Specify the order of this reaction with respect to $[\text{H}_2\text{O}_2]$ and $[\text{I}^-]$.
 b. Calculate the values of the rate constants, k_1 and k_2 .

- c. What reason could there be for the two-term dependence of the rate on $[\text{H}^+]$?

Integrative Problems

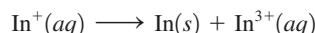
These problems require the integration of multiple concepts to find the solutions.

89. Sulfuryl chloride undergoes first-order decomposition at 320.°C with a half-life of 8.75 h.



What is the value of the rate constant, k , in s⁻¹? If the initial pressure of SO_2Cl_2 is 791 torr and the decomposition occurs in a 1.25-L container, how many molecules of SO_2Cl_2 remain after 12.5 h?

90. Upon dissolving $\text{InCl}(s)$ in HCl , $\text{In}^+(aq)$ undergoes a disproportionation reaction according to the following unbalanced equation:



This disproportionation follows first-order kinetics with a half-life of 667 s. What is the concentration of $\text{In}^+(aq)$ after 1.25 h if the initial solution of $\text{In}^+(aq)$ was prepared by dissolving 2.38 g of $\text{InCl}(s)$ in $5.00 \times 10^2 \text{ mL}$ of dilute HCl ? What mass of $\text{In}(s)$ is formed after 1.25 h?

91. The decomposition of iodoethane in the gas phase proceeds according to the following equation:



At 660. K, $k = 7.2 \times 10^{-4} \text{ s}^{-1}$; at 720. K, $k = 1.7 \times 10^{-2} \text{ s}^{-1}$. What is the rate constant for this first-order decomposition at 325°C? If the initial pressure of iodoethane is 894 torr at 245°C, what is the pressure of iodoethane after three half-lives?

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

92. Consider the following reaction:



At 25°C, the following two experiments were run, yielding the following data:

Experiment 1: $[\text{Y}]_0 = 3.0 \text{ M}$

$[\text{CH}_3\text{X}]$ (mol/L)	Time (h)
7.08×10^{-3}	1.0
4.52×10^{-3}	1.5
2.23×10^{-3}	2.3
4.76×10^{-4}	4.0
8.44×10^{-5}	5.7
2.75×10^{-5}	7.0

Experiment 2: $[Y]_0 = 4.5\text{ M}$

$[\text{CH}_3\text{X}] \text{ (mol/L)}$	Time (h)
4.50×10^{-3}	0
1.70×10^{-3}	1.0
4.19×10^{-4}	2.5
1.11×10^{-4}	4.0
2.81×10^{-5}	5.5

Experiments also were run at 85°C . The value of the rate constant at 85°C was found to be 7.88×10^8 (with the time in units of hours), where $[\text{CH}_3\text{X}]_0 = 1.0 \times 10^{-2}\text{ M}$ and $[Y]_0 = 3.0\text{ M}$.

- a. Determine the rate law and the value of k for this reaction at 25°C .

- b. Determine the half-life at 85°C .

- c. Determine E_a for the reaction.

- d. Given that the C—X bond energy is known to be about 325 kJ/mol, suggest a mechanism that explains the results in parts a and c.



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmc.com/PIC/zumdahl7e.

13 Chemical Equilibrium

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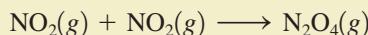
13.7 Le Châtelier's Principle

- The Effect of a Change in Concentration
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I

In doing stoichiometry calculations we assumed that reactions proceed to completion, that is, until one of the reactants runs out. Many reactions do proceed essentially to completion. For such reactions it can be assumed that the reactants are quantitatively converted to products and that the amount of limiting reactant that remains is negligible. On the other hand, there are many chemical reactions that stop far short of completion. An example is the dimerization of nitrogen dioxide:



The reactant, NO_2 , is a dark brown gas, and the product, N_2O_4 , is a colorless gas. When NO_2 is placed in an evacuated, sealed glass vessel at 25°C , the initial dark brown color decreases in intensity as it is converted to colorless N_2O_4 . However, even over a long period of time, the contents of the reaction vessel do not become colorless. Instead, the intensity of the brown color eventually becomes constant, which means that the concentration of NO_2 is no longer changing. This is illustrated on the molecular level in Fig. 13.1. This observation is a clear indication that the reaction has stopped short of completion. In fact, the system has reached **chemical equilibrium**, *the state where the concentrations of all reactants and products remain constant with time*.

Any chemical reactions carried out in a closed vessel will reach equilibrium. For some reactions the equilibrium position so favors the products that the reaction appears to have gone to completion. We say that the equilibrium position for such reactions lies *far to the right* (in the direction of the products). For example, when gaseous hydrogen and oxygen are mixed in stoichiometric quantities and react to form water vapor, the reaction proceeds essentially to completion. The amounts of the reactants that remain when the system reaches equilibrium are so tiny as to be negligible. By contrast, some reactions occur only to a slight extent. For example, when solid CaO is placed in a closed vessel at 25°C , the decomposition to solid Ca and gaseous O_2 is virtually undetectable. In cases like this, the equilibrium position is said to lie *far to the left* (in the direction of the reactants).

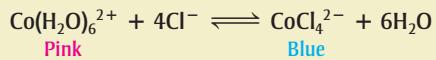
In this chapter we will discuss how and why a chemical system comes to equilibrium and the characteristics of equilibrium. In particular, we will discuss how to calculate the concentrations of the reactants and products present for a given system at equilibrium.

13.1 The Equilibrium Condition

Since no changes occur in the concentrations of reactants or products in a reaction system at equilibrium, it may appear that everything has stopped. However, this is not the case. On the molecular level, there is frantic activity. Equilibrium is not static but is a highly *dynamic* situation. The concept of chemical equilibrium is analogous to the flow of cars across a bridge connecting two island cities. Suppose the traffic flow on the bridge

Equilibrium is a dynamic situation.

The effect of temperature on the endothermic, aqueous equilibrium:



The violet solution in the center is at 25°C and contains significant quantities of both pink $\text{Co}(\text{H}_2\text{O})_6^{2+}$ and blue CoCl_4^{2-} . When the solution is cooled, it turns pink because the equilibrium is shifted to the left. Heating the solution favors the blue CoCl_4^{2-} ions.

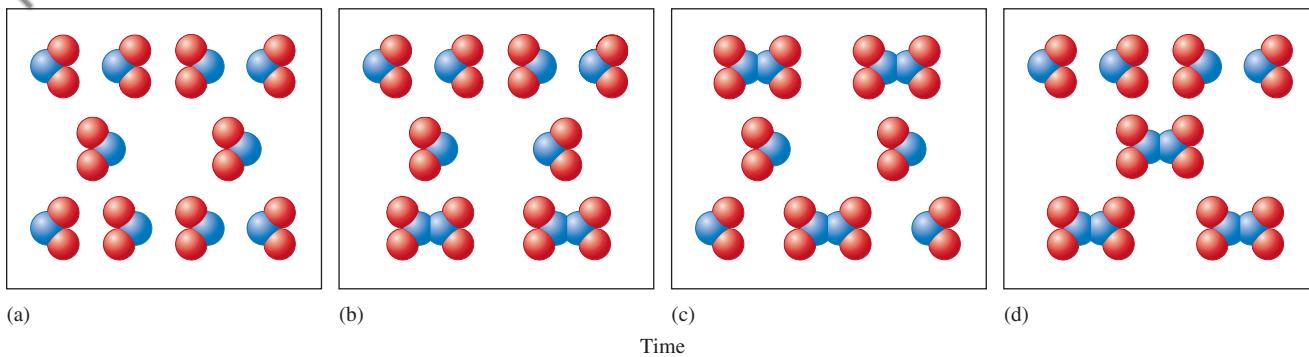


FIGURE 13.1

A molecular representation of the reaction $2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$ over time in a closed vessel. Note that the numbers of NO_2 and N_2O_4 in the container become constant (c and d) after sufficient time has passed.

is the same in both directions. It is obvious that there is motion, since one can see the cars traveling back and forth across the bridge, but the number of cars in each city is not changing because equal numbers of cars are entering and leaving. The result is no *net* change in the car population.

To see how this concept applies to chemical reactions, consider the reaction between steam and carbon monoxide in a closed vessel at a high temperature where the reaction takes place rapidly:



Assume that the same number of moles of gaseous CO and gaseous H₂O are placed in a closed vessel and allowed to react. The plots of the concentrations of reactants and products versus time are shown in Fig. 13.2. Note that since CO and H₂O were originally present in equal molar quantities, and since they react in a 1:1 ratio, the concentrations of the two gases are always equal. Also, since H₂ and CO₂ are formed in equal amounts, they are always present in the same concentrations.

Figure 13.2 is a profile of the progress of the reaction. When CO and H₂O are mixed, they immediately begin to react to form H₂ and CO₂. This leads to a decrease in the concentrations of the reactants, but the concentrations of the products, which were initially at zero, are increasing. Beyond a certain time, indicated by the dashed line in Fig. 13.2, the concentrations of reactants and products no longer change—equilibrium has been reached. Unless the system is somehow disturbed, no further changes in concentrations will occur. Note that although the equilibrium position lies far to the right, the concentrations of reactants never go to zero; the reactants will always be present in small but constant concentrations. This is shown on the microscopic level in Fig. 13.3.

What would happen to the gaseous equilibrium mixture of reactants and products represented in Fig. 13.3, parts (c) and (d), if we injected some $\text{H}_2\text{O}(g)$ into the box? To answer this question, we need to be sure we understand the equilibrium condition: The

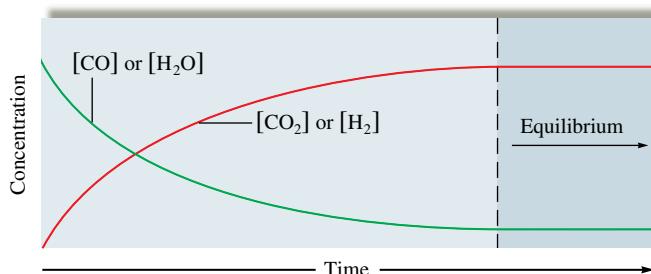
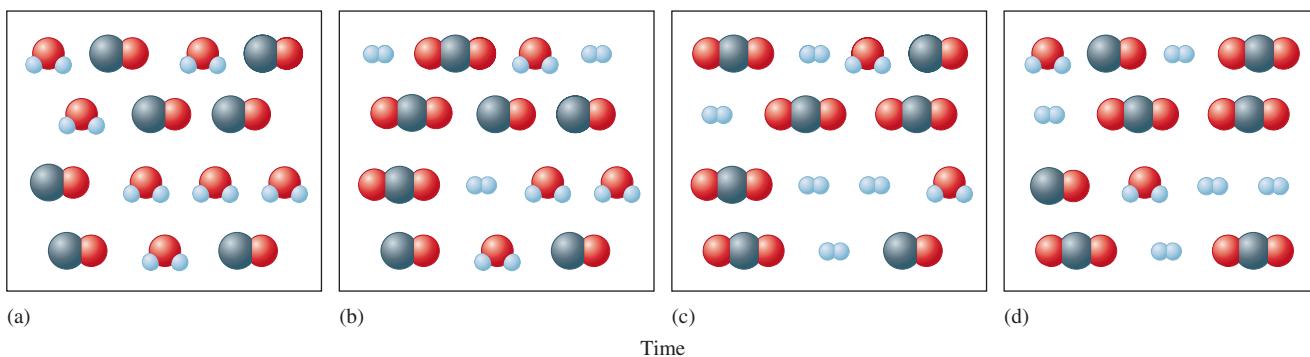


FIGURE 13.2

The changes in concentrations with time for the reaction $\text{H}_2\text{O}(g) + \text{CO}(g) \rightleftharpoons \text{H}_2(g) + \text{CO}_2(g)$ when equimolar quantities of $\text{H}_2\text{O}(g)$ and $\text{CO}(g)$ are mixed.

**FIGURE 13.3**

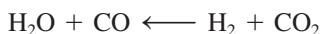
(a) H_2O and CO are mixed in equal numbers and begin to react (b) to form CO_2 and H_2 . After time has passed, equilibrium is reached (c) and the numbers of reactant and product molecules then remain constant over time (d).

concentrations of reactants and products remain constant at equilibrium because the forward and reverse reaction rates are equal. If we inject some H_2O molecules, what will happen to the forward reaction: $\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$? It will speed up because more H_2O molecules mean more collisions between H_2O and CO molecules. This in turn will form more products and will cause the reverse reaction $\text{H}_2\text{O} + \text{CO} \leftarrow \text{H}_2 + \text{CO}_2$ to speed up. Thus the system will change until the forward and reverse reaction rates again become equal. Will this new equilibrium position contain more or fewer product molecules than are shown in Fig. 13.3(c) and (d)? Think about this carefully. If you are not sure of the answer now, keep reading. We will consider this type of situation in more detail later in this chapter.

Why does equilibrium occur? We saw in Chapter 12 that molecules react by colliding with one another, and the more collisions, the faster the reaction. This is why reaction rates depend on concentrations. In this case the concentrations of H_2O and CO are lowered by the forward reaction:



As the concentrations of the reactants decrease, the forward reaction slows down (Fig. 13.4). As in the bridge traffic analogy, there is also a reverse direction:

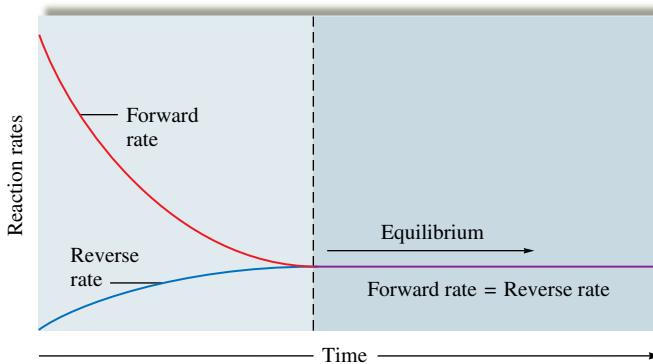


Initially in this experiment no H_2 and CO_2 were present, and this reverse reaction could not occur. However, as the forward reaction proceeds, the concentrations of H_2 and CO_2 build up, and the rate of the reverse reaction increases (Fig. 13.4) as the forward reaction slows down. Eventually, the concentrations reach levels where the rate of the forward reaction equals the rate of the reverse reaction. The system has reached equilibrium.

A double arrow (\rightleftharpoons) is used to show that a reaction can occur in either direction.

FIGURE 13.4

The changes with time in the rates of forward and reverse reactions for $\text{H}_2\text{O}(g) + \text{CO}(g) \rightleftharpoons \text{H}_2(g) + \text{CO}_2(g)$ when equimolar quantities of $\text{H}_2\text{O}(g)$ and $\text{CO}(g)$ are mixed. The rates do not change in the same way with time because the forward reaction has a much larger rate constant than the reverse reaction.

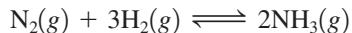


The relationship between equilibrium and thermodynamics is explored in Section 16.8.

The equilibrium position of a reaction—left, right, or somewhere in between—is determined by many factors: the initial concentrations, the relative energies of the reactants and products, and the relative degree of “organization” of the reactants and products. Energy and organization come into play because nature tries to achieve minimum energy and maximum disorder, as we will show in detail in Chapter 16. For now, we will simply view the equilibrium phenomenon in terms of the rates of opposing reactions.

The Characteristics of Chemical Equilibrium

To explore the important characteristics of chemical equilibrium, we will consider the synthesis of ammonia from elemental nitrogen and hydrogen:



The United States produces about 20 million tons of ammonia annually.

Molecules with strong bonds produce large activation energies and tend to react slowly at 25°C.

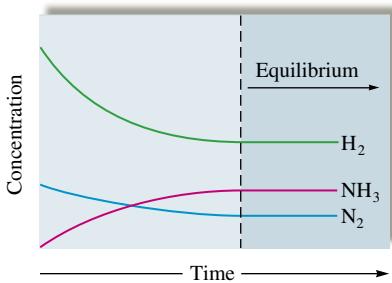


FIGURE 13.5
A concentration profile for the reaction $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$ when only $\text{N}_2(g)$ and $\text{H}_2(g)$ are mixed initially.

This process is of great commercial value because ammonia is an important fertilizer for the growth of corn and other crops. Ironically, this beneficial process was discovered in Germany just before World War I in a search for ways to produce nitrogen-based explosives. In the course of this work, German chemist Fritz Haber (1868–1934) pioneered the large-scale production of ammonia.

When gaseous nitrogen, hydrogen, and ammonia are mixed in a closed vessel at 25°C, no apparent change in the concentrations occurs over time, regardless of the original amounts of the gases. Why? There are two possible reasons why the concentrations of the reactants and products of a given chemical reaction remain unchanged when mixed.

1. The system is at chemical equilibrium.
2. The forward and reverse reactions are so slow that the system moves toward equilibrium at a rate that cannot be detected.

The second reason applies to the nitrogen, hydrogen, and ammonia mixture at 25°C. As we saw in Chapters 8 and 9, the N_2 molecule has a very strong triple bond (941 kJ/mol) and thus is very unreactive. Also, the H_2 molecule has an unusually strong single bond (432 kJ/mol). Therefore, mixtures of N_2 , H_2 , and NH_3 at 25°C can exist with no apparent change over long periods of time, unless a catalyst is introduced to speed up the forward and reverse reactions. Under appropriate conditions, the system does reach equilibrium, as shown in Fig. 13.5. Note that because of the reaction stoichiometry, H_2 disappears three times as fast as N_2 does and NH_3 forms twice as fast as N_2 disappears.

13.2 The Equilibrium Constant

Science is fundamentally empirical—it is based on experiment. The development of the equilibrium concept is typical. From their observations of many chemical reactions, two Norwegian chemists, Cato Maximilian Guldberg (1836–1902) and Peter Waage (1833–1900), proposed in 1864 the **law of mass action** as a general description of the equilibrium condition. Guldberg and Waage postulated that for a reaction of the type



where A, B, C, and D represent chemical species and j , k , l , and m are their coefficients in the balanced equation, the law of mass action is represented by the following **equilibrium expression**:

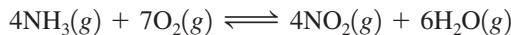
$$K = \frac{[\text{C}]^l [\text{D}]^m}{[\text{A}]^j [\text{B}]^k}$$

The square brackets indicate the concentrations of the chemical species *at equilibrium*, and K is a constant called the **equilibrium constant**.

The law of mass action is based on experimental observation.

Sample Exercise 13.1**Writing Equilibrium Expressions**

Write the equilibrium expression for the following reaction:

**Solution**

Applying the law of mass action gives

The square brackets indicate concentration in units of mol/L.

$$K = \frac{[\text{NO}_2]^4[\text{H}_2\text{O}]^6}{[\text{NH}_3]^4[\text{O}_2]^7}$$

See Exercise 13.17.

The value of the equilibrium constant at a given temperature can be calculated if we know the equilibrium concentrations of the reaction components, as illustrated in Sample Exercise 13.2.

It is very important to note at this point that the equilibrium constants are customarily given without units. The reason for this is beyond the scope of this text, but it involves corrections for the nonideal behavior of the substances taking part in the reaction. When these corrections are made, the units cancel out and the corrected K has no units. Thus we will not use units for K in this text.

Sample Exercise 13.2**Calculating the Values of K**

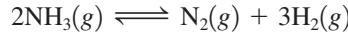
The following equilibrium concentrations were observed for the Haber process at 127°C:

$$[\text{NH}_3] = 3.1 \times 10^{-2} \text{ mol/L}$$

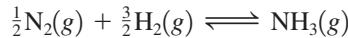
$$[\text{N}_2] = 8.5 \times 10^{-1} \text{ mol/L}$$

$$[\text{H}_2] = 3.1 \times 10^{-3} \text{ mol/L}$$

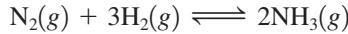
- Calculate the value of K at 127°C for this reaction.
- Calculate the value of the equilibrium constant at 127°C for the reaction



- Calculate the value of the equilibrium constant at 127°C for the reaction given by the equation

**Solution**

- The balanced equation for the Haber process is



Thus

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(3.1 \times 10^{-2})^2}{(8.5 \times 10^{-1})(3.1 \times 10^{-3})^3} \\ = 3.8 \times 10^4$$

Note that K is written without units.

- b. This reaction is written in the reverse order from the equation given in part a. This leads to the equilibrium expression

$$K' = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2}$$

which is the reciprocal of the expression used in part a. Therefore,

$$K' = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{1}{K} = \frac{1}{3.8 \times 10^4} = 2.6 \times 10^{-5}$$

- c. We use the law of mass action:

$$K'' = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}}$$

If we compare this expression to that obtained in part a, we see that since

$$\begin{aligned} \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}} &= \left(\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \right)^{1/2} \\ K'' &= K^{1/2} \end{aligned}$$

Thus

$$K'' = K^{1/2} = (3.8 \times 10^4)^{1/2} = 1.9 \times 10^2$$

See Exercises 13.19 and 13.21 through 13.24.

We can draw some important conclusions from the results of Sample Exercise 13.2. For a reaction of the form



the equilibrium expression is

$$K = \frac{[\text{C}]^l[\text{D}]^m}{[\text{A}]^j[\text{B}]^k}$$

If this reaction is reversed, then the new equilibrium expression is

$$K' = \frac{[\text{A}]^j[\text{B}]^k}{[\text{C}]^l[\text{D}]^m} = \frac{1}{K}$$

If the original reaction is multiplied by some factor n to give



the equilibrium expression becomes

$$K'' = \frac{[\text{C}]^{nl}[\text{D}]^{nm}}{[\text{A}]^{nj}[\text{B}]^{nk}} = K^n$$

We Can Summarize These Conclusions About the Equilibrium Expression as Follows:

- The equilibrium expression for a reaction is the reciprocal of that for the reaction written in reverse.
- When the balanced equation for a reaction is multiplied by a factor n , the equilibrium expression for the new reaction is the original expression raised to the n th power. Thus $K_{\text{new}} = (K_{\text{original}})^n$.
- K values are customarily written without units.

The law of mass action applies to solution and gaseous equilibria.



A cross section showing how anhydrous ammonia is injected into the soil to act as a fertilizer.

For a reaction at a given temperature, there are many equilibrium positions but only one value for K .

Sample Exercise 13.3

Equilibrium Positions

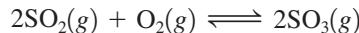
The following results were collected for two experiments involving the reaction at 600°C between gaseous sulfur dioxide and oxygen to form gaseous sulfur trioxide:

Experiment 1		Experiment 2	
Initial	Equilibrium	Initial	Equilibrium
$[\text{SO}_2]_0 = 2.00 \text{ M}$	$[\text{SO}_2] = 1.50 \text{ M}$	$[\text{SO}_2]_0 = 0.500 \text{ M}$	$[\text{SO}_2] = 0.590 \text{ M}$
$[\text{O}_2]_0 = 1.50 \text{ M}$	$[\text{O}_2] = 1.25 \text{ M}$	$[\text{O}_2]_0 = 0$	$[\text{O}_2] = 0.0450 \text{ M}$
$[\text{SO}_3]_0 = 3.00 \text{ M}$	$[\text{SO}_3] = 3.50 \text{ M}$	$[\text{SO}_3]_0 = 0.350 \text{ M}$	$[\text{SO}_3] = 0.260 \text{ M}$

Show that the equilibrium constant is the same in both cases.

Solution

The balanced equation for the reaction is



From the law of mass action,

$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

The law of mass action is widely applicable. It correctly describes the equilibrium behavior of an amazing variety of chemical systems in solution and in the gas phase. Although, as we will see later, corrections must be applied in certain cases, such as for concentrated aqueous solutions and for gases at high pressures, the law of mass action provides a remarkably accurate description of all types of chemical equilibria.

Consider again the ammonia synthesis reaction. The equilibrium constant K always has the same value at a given temperature. At 500°C the value of K is 6.0×10^{-2} . Whenever N₂, H₂, and NH₃ are mixed together at this temperature, the system will always come to an equilibrium position such that

$$\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 6.0 \times 10^{-2}$$

This expression has the same value at 500°C, regardless of the amounts of the gases that are mixed together initially.

Although the special ratio of products to reactants defined by the equilibrium expression is constant for a given reaction system at a given temperature, the *equilibrium concentrations will not always be the same*. Table 13.1 gives three sets of data for the synthesis of ammonia, showing that even though the individual sets of equilibrium concentrations are quite different for the different situations, the *equilibrium constant, which depends on the ratio of the concentrations, remains the same* (within experimental error). Note that subscript zeros indicate initial concentrations.

Each *set of equilibrium concentrations* is called an **equilibrium position**. It is essential to distinguish between the equilibrium constant and the equilibrium positions for a given reaction system. There is only *one* equilibrium constant for a particular system at a particular temperature, but there are an *infinite* number of equilibrium positions. The specific equilibrium position adopted by a system depends on the initial concentrations, but the equilibrium constant does not.

TABLE 13.1 Results of Three Experiments for the Reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$
I	$[N_2]_0 = 1.000 M$ $[H_2]_0 = 1.000 M$ $[NH_3]_0 = 0$	$[N_2] = 0.921 M$ $[H_2] = 0.763 M$ $[NH_3] = 0.157 M$	$K = 6.02 \times 10^{-2}$
II	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000 M$	$[N_2] = 0.399 M$ $[H_2] = 1.197 M$ $[NH_3] = 0.203 M$	$K = 6.02 \times 10^{-2}$
III	$[N_2]_0 = 2.00 M$ $[H_2]_0 = 1.00 M$ $[NH_3]_0 = 3.00 M$	$[N_2] = 2.59 M$ $[H_2] = 2.77 M$ $[NH_3] = 1.82 M$	$K = 6.02 \times 10^{-2}$

For Experiment 1,

$$K_1 = \frac{(3.50)^2}{(1.50)^2(1.25)} = 4.36$$

For Experiment 2,

$$K_2 = \frac{(0.260)^2}{(0.590)^2(0.0450)} = 4.32$$

The value of K is constant, within experimental error.

See Exercise 13.24.

13.3 Equilibrium Expressions Involving Pressures

So far we have been describing equilibria involving gases in terms of concentrations. Equilibria involving gases also can be described in terms of pressures. The relationship between the pressure and the concentration of a gas can be seen from the ideal gas equation:

$$PV = nRT \quad \text{or} \quad P = \left(\frac{n}{V}\right)RT = CRT$$

The ideal gas equation was discussed in Section 5.3.

where C equals n/V , or the number of moles n of gas per unit volume V . Thus C represents the *molar concentration of the gas*.

For the ammonia synthesis reaction, the equilibrium expression can be written in terms of concentrations, that is,

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{C_{NH_3}^2}{(C_{N_2})(C_{H_2}^3)} = K_c$$

or in terms of the *equilibrium partial pressures of the gases*, that is,

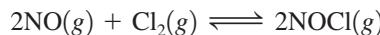
$$K_p = \frac{P_{NH_3}^2}{(P_{N_2})(P_{H_2}^3)}$$

K involves concentrations; K_p involves pressures. In some books, the symbol K_c is used instead of K .

Both the symbols K and K_c are used commonly for an equilibrium constant in terms of concentrations. We will always use K in this book. The symbol K_p represents an equilibrium constant in terms of partial pressures.

Sample Exercise 13.4**Calculating Values of K_p**

The reaction for the formation of nitrosyl chloride



was studied at 25°C. The pressures at equilibrium were found to be

$$P_{\text{NOCl}} = 1.2 \text{ atm}$$

$$P_{\text{NO}} = 5.0 \times 10^{-2} \text{ atm}$$

$$P_{\text{Cl}_2} = 3.0 \times 10^{-1} \text{ atm}$$

Calculate the value of K_p for this reaction at 25°C.

Solution

For this reaction,

$$\begin{aligned} K_p &= \frac{P_{\text{NOCl}}^2}{(P_{\text{NO}_2})^2(P_{\text{Cl}_2})} = \frac{(1.2)^2}{(5.0 \times 10^{-2})^2(3.0 \times 10^{-1})} \\ &= 1.9 \times 10^3 \end{aligned}$$

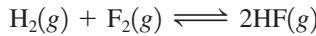
See Exercises 13.25 and 13.26.

The relationship between K and K_p for a particular reaction follows from the fact that for an ideal gas, $C = P/RT$. For example, for the ammonia synthesis reaction,

$$P = CRT \quad \text{or} \quad C = \frac{P}{RT}$$

$$\begin{aligned} K &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{C_{\text{NH}_3}^2}{(C_{\text{N}_2})(C_{\text{H}_2}^3)} \\ &= \frac{\left(\frac{P_{\text{NH}_3}}{RT}\right)^2}{\left(\frac{P_{\text{N}_2}}{RT}\right)\left(\frac{P_{\text{H}_2}}{RT}\right)^3} = \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)} \times \frac{\left(\frac{1}{RT}\right)^2}{\left(\frac{1}{RT}\right)^4} \\ &= \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)} (RT)^2 \\ &= K_p(RT)^2 \end{aligned}$$

However, for the synthesis of hydrogen fluoride from its elements,



the relationship between K and K_p is given by

$$\begin{aligned} K &= \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{C_{\text{HF}}^2}{(C_{\text{H}_2})(C_{\text{F}_2})} \\ &= \frac{\left(\frac{P_{\text{HF}}}{RT}\right)^2}{\left(\frac{P_{\text{H}_2}}{RT}\right)\left(\frac{P_{\text{F}_2}}{RT}\right)} = \frac{P_{\text{HF}}^2}{(P_{\text{H}_2})(P_{\text{F}_2})} \\ &= K_p \end{aligned}$$

Thus, for this reaction, K is equal to K_p . This equality occurs because the sum of the coefficients on either side of the balanced equation is identical, so the terms in RT cancel out. In the equilibrium expression for the ammonia synthesis reaction, the sum of the powers in the numerator is different from that in the denominator, and K does not equal K_p .

For the general reaction



the relationship between K and K_p is

$$K_p = K(RT)^{\Delta n}$$

where Δn is the sum of the coefficients of the *gaseous* products minus the sum of the coefficients of the *gaseous* reactants. This equation is quite easy to derive from the definitions of K and K_p and the relationship between pressure and concentration. For the preceding general reaction,

$$\begin{aligned} K_p &= \frac{(P_C)^l(P_D)^m}{(P_A)^j(P_B)^k} = \frac{(C_C \times RT)^l(C_D \times RT)^m}{(C_A \times RT)^j(C_B \times RT)^k} \\ &= \frac{(C_C)^l(C_D)^m}{(C_A)^j(C_B)^k} \times \frac{(RT)^{l+m}}{(RT)^{j+k}} = K(RT)^{(l+m)-(j+k)} \\ &= K(RT)^{\Delta n} \end{aligned}$$

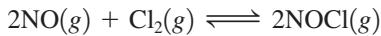
Δn always involves products minus reactants.

where $\Delta n = (l + m) - (j + k)$, the difference in the sums of the coefficients for the gaseous products and reactants.

Sample Exercise 13.5

Calculating K from K_p

Using the value of K_p obtained in Sample Exercise 13.4, calculate the value of K at 25°C for the reaction



Solution

From the value of K_p , we can calculate K using

$$K_p = K(RT)^{\Delta n}$$

where $T = 25 + 273 = 298$ K and

$$\Delta n = 2 - (2 + 1) = -1$$

↑
 Sum of
 product
 coefficients

↑
 Sum of
 reactant
 coefficients

$$\text{Thus } K_p = K(RT)^{-1} = \frac{K}{RT}$$

and

$$\begin{aligned} K &= K_p(RT) \\ &= (1.9 \times 10^3)(0.08206)(298) \\ &= 4.6 \times 10^4 \end{aligned}$$

See Exercises 13.27 and 13.28.

13.4 Heterogeneous Equilibria

So far we have discussed equilibria only for systems in the gas phase, where all reactants and products are gases. These are **homogeneous equilibria**. However, many equilibria involve more than one phase and are called **heterogeneous equilibria**. For example, the

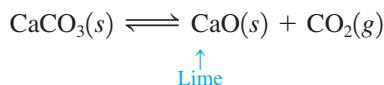
Lime is among the top five chemicals manufactured in the United States in terms of the amount produced.

The concentrations of pure liquids and solids are constant.



The Seven Sisters chalk cliffs in East Sussex, England. The chalk is made up of compressed calcium carbonate skeletons of microscopic algae from the late Cretaceous Period.

thermal decomposition of calcium carbonate in the commercial preparation of lime occurs by a reaction involving both solid and gas phases:



Straightforward application of the law of mass action leads to the equilibrium expression

$$K' = \frac{[\text{CO}_2][\text{CaO}]}{[\text{CaCO}_3]}$$

However, experimental results show that the *position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present* (see Fig. 13.6). The fundamental reason for this behavior is that the concentrations of pure solids and liquids cannot change. Thus the equilibrium expression for the decomposition of solid calcium carbonate might be represented as

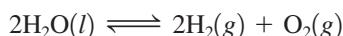
$$K' = \frac{[\text{CO}_2]C_1}{C_2}$$

where C_1 and C_2 are constants representing the concentrations of the solids CaO and CaCO₃, respectively. This expression can be rearranged to give

$$\frac{C_2 K'}{C_1} = K = [\text{CO}_2]$$

We can generalize from this result as follows: If pure solids or pure liquids are involved in a chemical reaction, their concentrations *are not included in the equilibrium expression* for the reaction. This simplification occurs *only* with pure solids or liquids, not with solutions or gases, since in these last two cases the concentrations can vary.

For example, in the decomposition of liquid water to gaseous hydrogen and oxygen,



where

$$K = [\text{H}_2]^2[\text{O}_2] \quad \text{and} \quad K_p = (P_{\text{H}_2})^2(P_{\text{O}_2})$$

water is not included in either equilibrium expression because it is a pure liquid. However, if the reaction were carried out under conditions where the water is a gas rather than a liquid, that is,

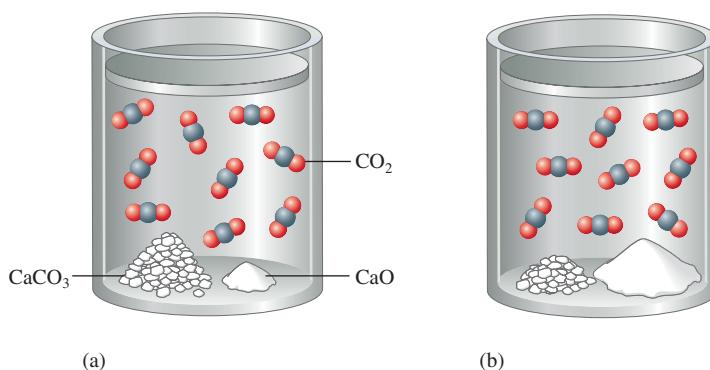
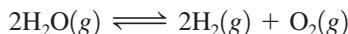


FIGURE 13.6

The position of the equilibrium $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$ does not depend on the amounts of $\text{CaCO}_3(s)$ and $\text{CaO}(s)$ present.

then

$$K = \frac{[\text{H}_2]^2[\text{O}_2]}{[\text{H}_2\text{O}]^2} \quad \text{and} \quad K_p = \frac{(P_{\text{H}_2})^2(P_{\text{O}_2})}{P_{\text{H}_2\text{O}}^2}$$

because the concentration or pressure of water vapor can change.

Sample Exercise 13.6

Equilibrium Expressions for Heterogeneous Equilibria

Write the expressions for K and K_p for the following processes:

- Solid phosphorus pentachloride decomposes to liquid phosphorus trichloride and chlorine gas.
- Deep blue solid copper(II) sulfate pentahydrate is heated to drive off water vapor to form white solid copper(II) sulfate.

Solution

- The reaction is

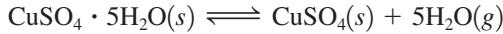


The equilibrium expressions are

$$K = [\text{Cl}_2] \quad \text{and} \quad K_p = P_{\text{Cl}_2}$$

In this case neither the pure solid PCl_5 nor the pure liquid PCl_3 is included in the equilibrium expressions.

- The reaction is



The equilibrium expressions are

$$K = [\text{H}_2\text{O}]^5 \quad \text{and} \quad K_p = (P_{\text{H}_2\text{O}})^5$$

The solids are not included.

See Exercise 13.29.

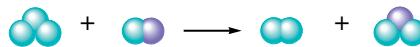


Hydrated copper(II) sulfate on the left.
Water applied to anhydrous copper(II)
sulfate, on the right, forms the hydrated
compound.

13.5 Applications of the Equilibrium Constant

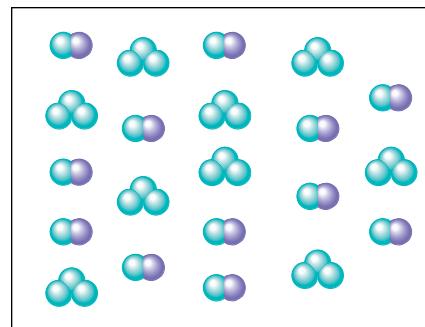
Knowing the equilibrium constant for a reaction allows us to predict several important features of the reaction: the tendency of the reaction to occur (but not the speed of the reaction), whether a given set of concentrations represents an equilibrium condition, and the equilibrium position that will be achieved from a given set of initial concentrations.

To introduce some of these ideas, we will first consider the reaction



where ○ and ○ represent two different types of atoms. Assume that this reaction has an equilibrium constant equal to 16.

In a given experiment, the two types of molecules are mixed together in the following amounts:



After the system reacts and comes to equilibrium, what will the system look like? We know that at equilibrium the ratio

$$\frac{(N_{\text{○}})(N_{\text{○}})}{(N_{\text{○}})(N_{\text{○}})} = 16$$

must be satisfied, where each N represents the number of molecules of each type. We originally have 9 ○ molecules and 12 ○ molecules. As a place to start, let's just assume that 5 ○ molecules disappear for the system to reach equilibrium. Since equal numbers of the ○ and ○ molecules react, this means that 5 ○ molecules also will disappear. This also means that 5 ○ molecules and 5 ○ molecules will be formed. We can summarize as follows:

Initial Conditions	New Conditions
9 ○ molecules	$9 - 5 = 4$ ○ molecules
12 ○ molecules	$12 - 5 = 7$ ○ molecules
0 ○ molecules	$0 + 5 = 5$ ○ molecules
0 ○ molecules	$0 + 5 = 5$ ○ molecules

Do the new conditions represent equilibrium for this reaction system? We can find out by taking the ratio of the numbers of molecules:

$$\frac{(N_{\text{○}})(N_{\text{○}})}{(N_{\text{○}})(N_{\text{○}})} = \frac{(5)(5)}{(4)(7)} = 0.9$$

Thus this is not an equilibrium position because the ratio is not 16, as required for equilibrium. In which direction must the system move to achieve equilibrium? Since the

observed ratio is smaller than 16, we must increase the numerator and decrease the denominator: The system needs to move to the right (toward more products) to achieve equilibrium. That is, more than 5 of the original reactant molecules must disappear to reach equilibrium for this system. How can we find the correct number? Since we do not know the number of molecules that need to disappear to reach equilibrium, let's call this number x . Now we can set up a table similar to the one we used earlier:

Initial Conditions	Equilibrium Conditions
9  molecules	x  disappear
12  molecules	x  disappear
0  molecules	x  form
0  molecules	x  form

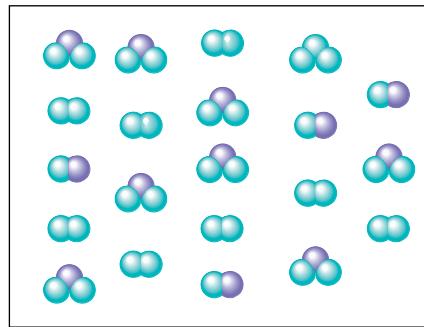
For the system to be at equilibrium, we know that the following ratio must be satisfied:

$$\frac{(N_{\text{O}_2})(N_{\text{N}_2O})}{(N_{\text{O}_2})(N_{\text{N}_2O})} = 16 = \frac{(x)(x)}{(9-x)(12-x)}$$

The easiest way to solve for x here is by trial and error. From our previous discussion we know that x is greater than 5. Also, we know that it must be less than 9 because we have only 9  molecules to start. We can't use all of them or we will have a zero in the denominator, which causes the ratio to be infinitely large. By trial and error, we find that $x = 8$ because

$$\frac{(x)(x)}{(9-x)(12-x)} = \frac{(8)(8)}{(9-8)(12-8)} = \frac{64}{4} = 16$$

The equilibrium mixture can be pictured as follows:

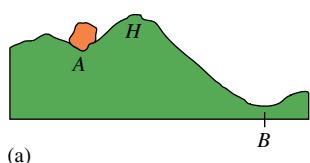


Note that it contains 8  molecules, 8  molecules, 1  molecule, and 4  molecules as required.

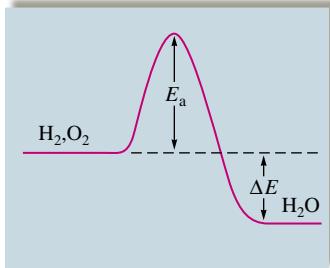
This pictorial example should help you understand the fundamental ideas of equilibrium. Now we will proceed to a more systematic quantitative treatment of chemical equilibrium.

The Extent of a Reaction

The inherent tendency for a reaction to occur is indicated by the magnitude of the equilibrium constant. A value of K much larger than 1 means that at equilibrium the reaction



(a)



(b)

FIGURE 13.7

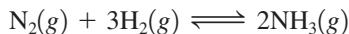
(a) A physical analogy illustrating the difference between thermodynamic and kinetic stabilities. The boulder is thermodynamically more stable (lower potential energy) in position B than in position A but cannot get over the hump H. (b) The reactants H_2 and O_2 have a strong tendency to form H_2O . That is, H_2O has lower energy than H_2 and O_2 . However, the large activation energy E_a prevents the reaction at 25°C. In other words, the magnitude of K for the reaction depends on ΔE , but the reaction rate depends on E_a .

system will consist of mostly products—the equilibrium lies to the right. Another way of saying this is that reactions with very large equilibrium constants go essentially to completion. On the other hand, a very small value of K means that the system at equilibrium will consist of mostly reactants—the equilibrium position is far to the left. The given reaction does not occur to any significant extent.

It is important to understand that *the size of K and the time required to reach equilibrium are not directly related*. The time required to achieve equilibrium depends on the reaction rate, which is determined by the size of the activation energy. The size of K is determined by thermodynamic factors such as the difference in energy between products and reactants. This difference is represented in Fig. 13.7 and will be discussed in detail in Chapter 16.

Reaction Quotient

When the reactants and products of a given chemical reaction are mixed, it is useful to know whether the mixture is at equilibrium or, if not, the direction in which the system must shift to reach equilibrium. If the concentration of one of the reactants or products is zero, the system will shift in the direction that produces the missing component. However, if all the initial concentrations are nonzero, it is more difficult to determine the direction of the move toward equilibrium. To determine the shift in such cases, we use the **reaction quotient, Q** . The reaction quotient is obtained by applying the law of mass action using *initial concentrations* instead of equilibrium concentrations. For example, for the synthesis of ammonia



the expression for the reaction quotient is

$$Q = \frac{[\text{NH}_3]^2}{[\text{N}_2]_0[\text{H}_2]^3}$$

where the subscript zeros indicate initial concentrations.

To determine in which direction a system will shift to reach equilibrium, we compare the values of Q and K . There are three possible cases:

- Q is equal to K .* The system is at equilibrium; no shift will occur.
- Q is greater than K .* In this case, the ratio of initial concentrations of products to initial concentrations of reactants is too large. To reach equilibrium, a net change of products to reactants must occur. The system *shifts to the left*, consuming products and forming reactants, until equilibrium is achieved.
- Q is less than K .* In this case, the ratio of initial concentrations of products to initial concentrations of reactants is too small. The system *must shift to the right*, consuming reactants and forming products, to attain equilibrium.

Sample Exercise 13.7

Using the Reaction Quotient

For the synthesis of ammonia at 500°C, the equilibrium constant is 6.0×10^{-2} . Predict the direction in which the system will shift to reach equilibrium in each of the following cases:

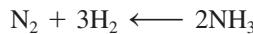
- $[\text{NH}_3]_0 = 1.0 \times 10^{-3} M$; $[\text{N}_2]_0 = 1.0 \times 10^{-5} M$; $[\text{H}_2]_0 = 2.0 \times 10^{-3} M$
- $[\text{NH}_3]_0 = 2.00 \times 10^{-4} M$; $[\text{N}_2]_0 = 1.50 \times 10^{-5} M$; $[\text{H}_2]_0 = 3.54 \times 10^{-1} M$
- $[\text{NH}_3]_0 = 1.0 \times 10^{-4} M$; $[\text{N}_2]_0 = 5.0 M$; $[\text{H}_2]_0 = 1.0 \times 10^{-2} M$

Solution

- a. First we calculate the value of Q :

$$Q = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{(1.0 \times 10^{-3})^2}{(1.0 \times 10^{-5})(2.0 \times 10^{-3})^3} \\ = 1.3 \times 10^7$$

Since $K = 6.0 \times 10^{-2}$, Q is much greater than K . To attain equilibrium, the concentrations of the products must be decreased and the concentrations of the reactants increased. The system will shift to the left:



- b. We calculate the value of Q :

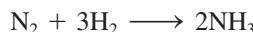
$$Q = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{(2.00 \times 10^{-4})^2}{(1.50 \times 10^{-5})(3.54 \times 10^{-1})^3} \\ = 6.01 \times 10^{-2}$$

In this case $Q = K$, so the system is at equilibrium. No shift will occur.

- c. The value of Q is

$$Q = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{(1.0 \times 10^{-4})^2}{(5.0)(1.0 \times 10^{-2})^3} \\ = 2.0 \times 10^{-3}$$

Here Q is less than K , so the system will shift to the right to attain equilibrium by increasing the concentration of the product and decreasing the reactant concentrations:



See Exercises 13.33 through 13.36.

Calculating Equilibrium Pressures and Concentrations

A typical equilibrium problem involves finding the equilibrium concentrations (or pressures) of reactants and products, given the value of the equilibrium constant and the initial concentrations (or pressures). However, since such problems sometimes become complicated mathematically, we will develop useful strategies for solving them by considering cases for which we know one or more of the equilibrium concentrations (or pressures).

Sample Exercise 13.8

Calculating Equilibrium Pressures I

Dinitrogen tetroxide in its liquid state was used as one of the fuels on the lunar lander for the NASA Apollo missions. In the gas phase it decomposes to gaseous nitrogen dioxide:



Consider an experiment in which gaseous N_2O_4 was placed in a flask and allowed to reach equilibrium at a temperature where $K_p = 0.133$. At equilibrium, the pressure of N_2O_4 was found to be 2.71 atm. Calculate the equilibrium pressure of $\text{NO}_2(g)$.



Apollo II lunar landing module at Tranquility Base, 1969.

Solution

We know that the equilibrium pressures of the gases NO_2 and N_2O_4 must satisfy the relationship

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = 0.133$$

Since we know $P_{\text{N}_2\text{O}_4}$, we can simply solve for P_{NO_2} :

$$P_{\text{NO}_2}^2 = K_p(P_{\text{N}_2\text{O}_4}) = (0.133)(2.71) = 0.360$$

Therefore,

$$P_{\text{NO}_2} = \sqrt{0.360} = 0.600$$

See Exercises 13.37 and 13.38.

Sample Exercise 13.9

Calculating Equilibrium Pressures II

At a certain temperature a 1.00-L flask initially contained 0.298 mol $\text{PCl}_3(g)$ and 8.70×10^{-3} mol $\text{PCl}_5(g)$. After the system had reached equilibrium, 2.00×10^{-3} mol $\text{Cl}_2(g)$ was found in the flask. Gaseous PCl_5 decomposes according to the reaction



Calculate the equilibrium concentrations of all species and the value of K .

Solution

The equilibrium expression for this reaction is

$$K = \frac{[\text{Cl}_2][\text{PCl}_3]}{[\text{PCl}_5]}$$

To find the value of K , we must calculate the equilibrium concentrations of all species and then substitute these quantities into the equilibrium expression. The best method for finding the equilibrium concentrations is to begin with the initial concentrations, which we will define as the concentrations before any shift toward equilibrium has occurred. We will then modify these initial concentrations appropriately to find the equilibrium concentrations.

The initial concentrations are

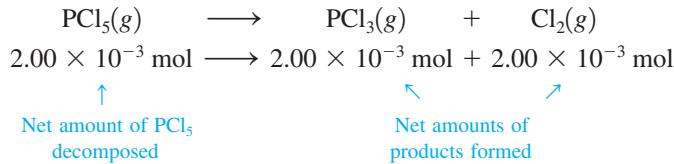
$$[\text{Cl}_2]_0 = 0$$

$$[\text{PCl}_3]_0 = \frac{0.298 \text{ mol}}{1.00 \text{ L}} = 0.298 \text{ M}$$

$$[\text{PCl}_5]_0 = \frac{8.70 \times 10^{-3} \text{ mol}}{1.00 \text{ L}} = 8.70 \times 10^{-3} \text{ M}$$

Next we find the change required to reach equilibrium. Since no Cl_2 was initially present but $2.00 \times 10^{-3} \text{ M}$ Cl_2 is present at equilibrium, 2.00×10^{-3} mol PCl_5 must have

decomposed to form 2.00×10^{-3} mol Cl_2 and 2.00×10^{-3} mol PCl_3 . In other words, to reach equilibrium, the reaction shifted to the right:



Now we apply this change to the initial concentrations to obtain the equilibrium concentrations:

$$[\text{Cl}_2] = 0 + \frac{2.00 \times 10^{-3} \text{ mol}}{1.00 \text{ L}} = 2.00 \times 10^{-3} M$$

$([\text{Cl}_2]_0)$

$$[\text{PCl}_3] = 0.298 M + \frac{2.00 \times 10^{-3} \text{ mol}}{1.00 \text{ L}} = 0.300 M$$

$([\text{PCl}_3]_0)$

$$[\text{PCl}_5] = 8.70 \times 10^{-3} M - \frac{2.00 \times 10^{-3} \text{ mol}}{1.00 \text{ L}} = 6.70 \times 10^{-3} M$$

$([\text{PCl}_5]_0)$

These equilibrium concentrations can now be used to find K :

$$K = \frac{[\text{Cl}_2][\text{PCl}_3]}{[\text{PCl}_5]} = \frac{(2.00 \times 10^{-3})(0.300)}{6.70 \times 10^{-3}}$$

$$= 8.96 \times 10^{-2}$$

See Exercises 13.39 through 13.42.

Sometimes we are not given any of the equilibrium concentrations (or pressures), only the initial values. Then we must use the stoichiometry of the reaction to express concentrations (or pressures) at equilibrium in terms of the initial values. This is illustrated in Sample Exercise 13.10.

Sample Exercise 13.10

Calculating Equilibrium Concentrations I

Carbon monoxide reacts with steam to produce carbon dioxide and hydrogen. At 700 K the equilibrium constant is 5.10. Calculate the equilibrium concentrations of all species if 1.000 mol of each component is mixed in a 1.000-L flask.

Solution

The balanced equation for the reaction is



and

$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = 5.10$$

Next we calculate the initial concentrations:

$$[\text{CO}]_0 = [\text{H}_2\text{O}]_0 = [\text{CO}_2]_0 = [\text{H}_2]_0 = \frac{1.000 \text{ mol}}{1.000 \text{ L}} = 1.000 M$$

Is the system at equilibrium, and if not, which way will it shift to reach the equilibrium position? These questions can be answered by calculating Q :

$$Q = \frac{[\text{CO}_2]_0[\text{H}_2]_0}{[\text{CO}]_0[\text{H}_2\text{O}]_0} = \frac{(1.000 \text{ mol/L})(1.000 \text{ mol/L})}{(1.000 \text{ mol/L})(1.000 \text{ mol/L})} = 1.000$$

Since Q is less than K , the system is not at equilibrium initially but must shift to the right.

What are the equilibrium concentrations? As before, we start with the initial concentrations and modify them to obtain the equilibrium concentrations. We must ask this question: How much will the system shift to the right to attain the equilibrium condition? In Sample Exercise 13.9 the change needed for the system to reach equilibrium was given. However, in this case we do not have this information.

Since the required change in concentrations is unknown at this point, we will define it in terms of x . Let's assume that x mol/L CO must react for the system to reach equilibrium. This means that the initial concentration of CO will decrease by x mol/L:

$$\begin{array}{c} [\text{CO}] = [\text{CO}]_0 - x \\ \uparrow \quad \uparrow \quad \uparrow \\ \text{Equilibrium} \quad \text{Initial} \quad \text{Change} \end{array}$$

Since each CO molecule reacts with one H₂O molecule, the concentration of water vapor also must decrease by x mol/L:

$$[\text{H}_2\text{O}] = [\text{H}_2\text{O}]_0 - x$$

As the reactant concentrations decrease, the product concentrations increase. Since all the coefficients are 1 in the balanced reaction, 1 mol CO reacting with 1 mol H₂O will produce 1 mol CO₂ and 1 mol H₂. Or in the present case, to reach equilibrium, x mol/L CO will react with x mol/L H₂O to give an additional x mol/L CO₂ and x mol/L H₂:



Thus the initial concentrations of CO₂ and H₂ will increase by x mol/L:

$$\begin{aligned} [\text{CO}_2] &= [\text{CO}_2]_0 + x \\ [\text{H}_2] &= [\text{H}_2]_0 + x \end{aligned}$$

Now we have all the equilibrium concentrations defined in terms of the initial concentrations and the change x :

Initial Concentration (mol/L)	Change (mol/L)	Equilibrium Concentration (mol/L)
[\text{CO}] ₀ = 1.000	- x	1.000 - x
[\text{H}_2\text{O}] ₀ = 1.000	- x	1.000 - x
[\text{CO}_2] ₀ = 1.000	+ x	1.000 + x
[\text{H}_2] ₀ = 1.000	+ x	1.000 + x

Note that the sign of x is determined by the direction of the shift. In this example, the system shifts to the right, so the product concentrations increase and the reactant concentrations decrease. Also note that because the coefficients in the balanced equation are all 1, the magnitude of the change is the same for all species.

Now since we know that the equilibrium concentrations must satisfy the equilibrium expression, we can find the value of x by substituting these concentrations into the expression

$$K = 5.10 = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(1.000 + x)(1.000 + x)}{(1.000 - x)(1.000 - x)} = \frac{(1.000 + x)^2}{(1.000 - x)^2}$$

Since the right side of the equation is a perfect square, the solution of the problem can be simplified by taking the square root of both sides:

$$\sqrt{5.10} = 2.26 = \frac{1.000 + x}{1.000 - x}$$

Multiplying and collecting terms gives

$$x = 0.387 \text{ mol/L}$$

Thus the system shifts to the right, consuming 0.387 mol/L CO and 0.387 mol/L H₂O and forming 0.387 mol/L CO₂ and 0.387 mol/L H₂.

Now the equilibrium concentrations can be calculated:

$$\begin{aligned} [\text{CO}] &= [\text{H}_2\text{O}] = 1.000 - x = 1.000 - 0.387 = 0.613 \text{ M} \\ [\text{CO}_2] &= [\text{H}_2] = 1.000 + x = 1.000 + 0.387 = 1.387 \text{ M} \end{aligned}$$

Reality Check: These values can be checked by substituting them back into the equilibrium expression to make sure they give the correct value for *K*:

$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(1.387)^2}{(0.613)^2} = 5.12$$

This result is the same as the given value of *K* (5.10) within round-off error, so the answer must be correct.

See Exercise 13.45.

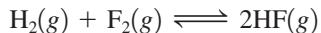
Sample Exercise 13.11

Calculating Equilibrium Concentrations II

Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of 1.15×10^2 at a certain temperature. In a particular experiment, 3.000 mol of each component was added to a 1.500-L flask. Calculate the equilibrium concentrations of all species.

Solution

The balanced equation for the reaction is



The equilibrium expression is

$$K = 1.15 \times 10^2 = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]}$$

We first calculate the initial concentrations:

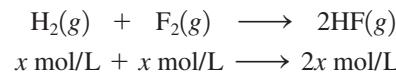
$$[\text{HF}]_0 = [\text{H}_2]_0 = [\text{F}_2]_0 = \frac{3.000 \text{ mol}}{1.500 \text{ L}} = 2.000 \text{ M}$$

Then we find the value of *Q*:

$$Q = \frac{[\text{HF}]_0^2}{[\text{H}_2]_0[\text{F}_2]_0} = \frac{(2.000)^2}{(2.000)(2.000)} = 1.000$$

Since *Q* is much less than *K*, the system must shift to the right to reach equilibrium.

What change in the concentrations is necessary? Since this is presently unknown, we will define the change needed in terms of x . Let x equal the number of moles per liter of H_2 consumed to reach equilibrium. The stoichiometry of the reaction shows that x mol/L F_2 also will be consumed and $2x$ mol/L HF will be formed:



Now the equilibrium concentrations can be expressed in terms of x :

Initial Concentration (mol/L)	Change (mol/L)	Equilibrium Concentration (mol/L)
$[\text{H}_2]_0 = 2.000$	$-x$	$[\text{H}_2] = 2.000 - x$
$[\text{F}_2]_0 = 2.000$	$-x$	$[\text{F}_2] = 2.000 - x$
$[\text{HF}]_0 = 2.000$	$+2x$	$[\text{HF}] = 2.000 + 2x$

These concentrations can be represented in a shorthand table as follows:

	$\text{H}_2(g)$	+	$\text{F}_2(g)$	\rightleftharpoons	$2\text{HF}(g)$
Initial:	2.000		2.000		2.000
Change:	$-x$		$-x$		$+2x$
Equilibrium:	$2.000 - x$		$2.000 - x$		$2.000 + 2x$

To solve for x , we substitute the equilibrium concentrations into the equilibrium expression:

$$K = 1.15 \times 10^2 = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(2.000 + 2x)^2}{(2.000 - x)^2}$$

The right side of this equation is a perfect square, so taking the square root of both sides gives

$$\sqrt{1.15 \times 10^2} = \frac{2.000 + 2x}{2.000 - x}$$

which yields $x = 1.528$. The equilibrium concentrations can now be calculated:

$$\begin{aligned} [\text{H}_2] &= [\text{F}_2] = 2.000 M - x = 0.472 M \\ [\text{HF}] &= 2.000 M + 2x = 5.056 M \end{aligned}$$

Reality Check: Checking these values by substituting them into the equilibrium expression gives

$$\frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(5.056)^2}{(0.472)^2} = 1.15 \times 10^2$$

which agrees with the given value of K .

See Exercise 13.46.

13.6 Solving Equilibrium Problems

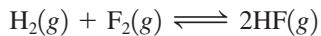
We have already considered most of the strategies needed to solve equilibrium problems. The typical procedure for analyzing a chemical equilibrium problem can be summarized as follows:

Procedure for Solving Equilibrium Problems

- 1 Write the balanced equation for the reaction.
- 2 Write the equilibrium expression using the law of mass action.
- 3 List the initial concentrations.
- 4 Calculate Q , and determine the direction of the shift to equilibrium.
- 5 Define the change needed to reach equilibrium, and define the equilibrium concentrations by applying the change to the initial concentrations.
- 6 Substitute the equilibrium concentrations into the equilibrium expression, and solve for the unknown.
- 7 Check your calculated equilibrium concentrations by making sure they give the correct value of K .

So far we have been careful to choose systems in which we can solve for the unknown by taking the square root of both sides of the equation. However, this type of system is not really very common, and we must now consider a more typical problem. Suppose for a synthesis of hydrogen fluoride from hydrogen and fluorine, 3.000 mol H_2 and 6.000 mol F_2 are mixed in a 3.000-L flask. Assume that the equilibrium constant for the synthesis reaction at this temperature is 1.15×10^2 . We calculate the equilibrium concentration of each component as follows:

- 1 We begin, as usual, by writing the balanced equation for the reaction:



- 2 The equilibrium expression is

$$K = 1.15 \times 10^2 = \frac{[HF]^2}{[H_2][F_2]}$$

- 3 The initial concentrations are

$$[H_2]_0 = \frac{3.000 \text{ mol}}{3.000 \text{ L}} = 1.000 M$$

$$[F_2]_0 = \frac{6.000 \text{ mol}}{3.000 \text{ L}} = 2.000 M$$

$$[HF]_0 = 0$$

- 4 There is no need to calculate Q because no HF is present initially, and we know that the system must shift to the right to reach equilibrium.

- 5 If we let x represent the number of moles per liter of H_2 consumed to reach equilibrium, we can represent the equilibrium concentrations as follows:

	$H_2(g)$	+	$F_2(g)$	\rightleftharpoons	$2HF(g)$
Initial:	1.000		2.000		0
Change:	$-x$		$-x$		$+2x$
Equilibrium:	$1.000 - x$		$2.000 - x$		$2x$

→ 6 Substituting the equilibrium concentrations into the equilibrium expression gives

$$K = 1.15 \times 10^2 = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)}$$

Since the right side of this equation is not a perfect square, we cannot take the square root of both sides, but must use some other procedure.

First, do the indicated multiplication:

$$(1.000 - x)(2.000 - x)(1.15 \times 10^2) = (2x)^2$$

$$\text{or } (1.15 \times 10^2)x^2 - 3.000(1.15 \times 10^2)x + 2.000(1.15 \times 10^2) = 4x^2$$

and collect terms

$$(1.11 \times 10^2)x^2 - (3.45 \times 10^2)x + 2.30 \times 10^2 = 0$$

This is a quadratic equation of the general form

$$ax^2 + bx + c = 0$$

Use of the quadratic formula is explained in Appendix 1.4.

where the roots can be obtained from the quadratic formula:

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

In this example, $a = 1.11 \times 10^2$, $b = -3.45 \times 10^2$, and $c = 2.30 \times 10^2$. Substituting these values into the quadratic formula gives two values for x :

$$x = 2.14 \text{ mol/L} \quad \text{and} \quad x = 0.968 \text{ mol/L}$$

Both these results cannot be valid (since a *given* set of initial concentrations leads to only *one* equilibrium position). How can we choose between them? Since the expression for the equilibrium concentration of H_2 is

$$[\text{H}_2] = 1.000 M - x$$

the value of x cannot be 2.14 mol/L (because subtracting 2.14 M from 1.000 M gives a negative concentration of H_2 , which is physically impossible). Thus the correct value for x is 0.968 mol/L, and the equilibrium concentrations are as follows:

$$\begin{aligned} [\text{H}_2] &= 1.000 M - 0.968 M = 3.2 \times 10^{-2} M \\ [\text{F}_2] &= 2.000 M - 0.968 M = 1.032 M \\ [\text{HF}] &= 2(0.968 M) = 1.936 M \end{aligned}$$

Reality Check:

→ 7 We can check these concentrations by substituting them into the equilibrium expression:

$$\frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(1.936)^2}{(3.2 \times 10^{-2})(1.032)} = 1.13 \times 10^2$$

This value is in close agreement with the given value for K (1.15×10^2), so the calculated equilibrium concentrations are correct.

This procedure is further illustrated for a problem involving pressures in Sample Exercise 13.12.

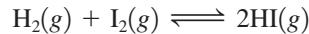
Sample Exercise 13.12

Calculating Equilibrium Pressures

Assume that gaseous hydrogen iodide is synthesized from hydrogen gas and iodine vapor at a temperature where the equilibrium constant is 1.00×10^2 . Suppose HI at 5.000×10^{-1} atm, H_2 at 1.000×10^{-2} atm, and I_2 at 5.000×10^{-3} atm are mixed in a 5.000-L flask. Calculate the equilibrium pressures of all species.

Solution

The balanced equation for this process is



and the equilibrium expression in terms of pressure is

$$K_p = \frac{P_{\text{HI}}^2}{(P_{\text{H}_2})(P_{\text{I}_2})} = 1.00 \times 10^2$$

The given initial pressures are

$$P_{\text{HI}}^0 = 5.000 \times 10^{-1} \text{ atm}$$

$$P_{\text{H}_2}^0 = 1.000 \times 10^{-2} \text{ atm}$$

$$P_{\text{I}_2}^0 = 5.000 \times 10^{-3} \text{ atm}$$

The value of Q for this system is

$$Q = \frac{(P_{\text{HI}}^0)^2}{(P_{\text{H}_2}^0)(P_{\text{I}_2}^0)} = \frac{(5.000 \times 10^{-1} \text{ atm})^2}{(1.000 \times 10^{-2} \text{ atm})(5.000 \times 10^{-3} \text{ atm})} = 5.000 \times 10^3$$

Since Q is greater than K , the system will shift to the left to reach equilibrium.

So far we have used moles or concentrations in stoichiometric calculations. However, it is equally valid to use pressures for a gas-phase system at constant temperature and volume because in this case pressure is directly proportional to the number of moles:

$$P = n \left(\frac{RT}{V} \right) \xleftarrow{\text{Constant if constant } T \text{ and } V}$$

Thus we can represent the change needed to achieve equilibrium in terms of pressures.

Let x be the change in pressure (in atm) of H_2 as the system shifts left toward equilibrium. This leads to the following equilibrium pressures:

	$\text{H}_2(g)$	$+$	$\text{I}_2(g)$	\rightleftharpoons	$2\text{HI}(g)$
Initial:	1.000×10^{-2}		5.000×10^{-3}		5.000×10^{-1}
Change:	$+x$		$+x$		$-2x$
Equilibrium:	$1.000 \times 10^{-2} + x$		$5.000 \times 10^{-3} + x$		$5.000 \times 10^{-1} - 2x$

Substitution into the equilibrium expression gives

$$K_p = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})} = \frac{(5.000 \times 10^{-1} - 2x)^2}{(1.000 \times 10^{-2} + x)(5.000 \times 10^{-3} + x)}$$

Multiplying and collecting terms yield the quadratic equation where $a = 9.60 \times 10^1$, $b = 3.5$, and $c = -2.45 \times 10^{-1}$:

$$(9.60 \times 10^1)x^2 + 3.5x - (2.45 \times 10^{-1}) = 0$$

From the quadratic formula, the correct value for x is $x = 3.55 \times 10^{-2}$ atm. The equilibrium pressures can now be calculated from the expressions involving x :

$$P_{\text{HI}} = 5.000 \times 10^{-1} \text{ atm} - 2(3.55 \times 10^{-2}) \text{ atm} = 4.29 \times 10^{-1} \text{ atm}$$

$$P_{\text{H}_2} = 1.000 \times 10^{-2} \text{ atm} + 3.55 \times 10^{-2} \text{ atm} = 4.55 \times 10^{-2} \text{ atm}$$

$$P_{\text{I}_2} = 5.000 \times 10^{-3} \text{ atm} + 3.55 \times 10^{-2} \text{ atm} = 4.05 \times 10^{-2} \text{ atm}$$

Reality Check:

$$\frac{P_{\text{HI}}^2}{P_{\text{H}_2} \cdot P_{\text{I}_2}} = \frac{(4.29 \times 10^{-1})^2}{(4.55 \times 10^{-2})(4.05 \times 10^{-2})} = 99.9$$

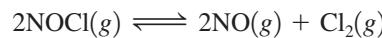
This agrees with the given value of K (1.00×10^2), so the calculated equilibrium concentrations are correct.

See Exercises 13.47 through 13.50.

Treating Systems That Have Small Equilibrium Constants

We have seen that fairly complicated calculations are often necessary to solve equilibrium problems. However, under certain conditions, simplifications are possible that greatly reduce the mathematical difficulties. For example, gaseous NOCl decomposes to form the gases NO and Cl_2 . At 35°C the equilibrium constant is 1.6×10^{-5} . In an experiment in which 1.0 mol NOCl is placed in a 2.0-L flask, what are the equilibrium concentrations?

The balanced equation is



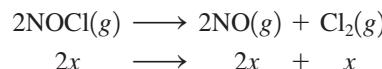
and

$$K = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = 1.6 \times 10^{-5}$$

The initial concentrations are

$$[\text{NOCl}]_0 = \frac{1.0 \text{ mol}}{2.0 \text{ L}} = 0.50 \text{ M} \quad [\text{NO}]_0 = 0 \quad [\text{Cl}_2]_0 = 0$$

Since there are no products initially, the system will move to the right to reach equilibrium. We will define x as the change in concentration of Cl_2 needed to reach equilibrium. The changes in the concentrations of NOCl and NO can then be obtained from the balanced equation:



The concentrations can be summarized as follows:

	$2\text{NOCl}(g)$	\rightleftharpoons	$2\text{NO}(g)$	$+$	$\text{Cl}_2(g)$
Initial:	0.50		0		0
Change:	$-2x$		$+2x$		$+x$
Equilibrium:	$0.50 - 2x$		$2x$		x

The equilibrium concentrations must satisfy the equilibrium expression

$$K = 1.6 \times 10^{-5} = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(2x)^2(x)}{(0.50 - 2x)^2}$$

Multiplying and collecting terms will give an equation with terms containing x^3 , x^2 , and x , which requires complicated methods to solve directly. However, we can avoid this situation by recognizing that since K is so small (1.6×10^{-5}), the system will not proceed far to the right to reach equilibrium. That is, x represents a relatively small number. The consequence of this fact is that the term $(0.50 - 2x)$ can be approximated by 0.50. That is, when x is small,

$$0.50 - 2x \approx 0.50$$

Approximations can simplify complicated math, but their validity should be checked carefully.

Making this approximation allows us to simplify the equilibrium expression:

$$1.6 \times 10^{-5} = \frac{(2x)^2(x)}{(0.50 - 2x)^2} \approx \frac{(2x)^2(x)}{(0.50)^2} = \frac{4x^3}{(0.50)^2}$$

Solving for x^3 gives

$$x^3 = \frac{(1.6 \times 10^{-5})(0.50)^2}{4} = 1.0 \times 10^{-6}$$

and $x = 1.0 \times 10^{-2}$.

How valid is this approximation? If $x = 1.0 \times 10^{-2}$, then

$$0.50 - 2x = 0.50 - 2(1.0 \times 10^{-2}) = 0.48$$

The difference between 0.50 and 0.48 is 0.02, or 4% of the initial concentration of NOCl, a relatively small discrepancy that will have little effect on the outcome. That is, since $2x$ is very small compared with 0.50, the value of x obtained in the approximate solution should be very close to the exact value. We use this approximate value of x to calculate the equilibrium concentrations:

$$[\text{NOCl}] = 0.50 - 2x \approx 0.50 M$$

$$[\text{NO}] = 2x = 2(1.0 \times 10^{-2} M) = 2.0 \times 10^{-2} M$$

$$[\text{Cl}_2] = x = 1.0 \times 10^{-2} M$$

Reality Check:

$$\frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(2.0 \times 10^{-2})^2(1.0 \times 10^{-2})}{(0.50)^2} = 1.6 \times 10^{-5}$$

Since the given value of K is 1.6×10^{-5} , these calculated concentrations are correct.

This problem was much easier to solve than it appeared at first because the *small value of K and the resulting small shift to the right to reach equilibrium allowed simplification*.

13.7 Le Châtelier's Principle

It is important to understand the factors that control the *position* of a chemical equilibrium. For example, when a chemical is manufactured, the chemists and chemical engineers in charge of production want to choose conditions that favor the desired product as much as possible. That is, they want the equilibrium to lie far to the right. When Fritz Haber was developing the process for the synthesis of ammonia, he did extensive studies on how temperature and pressure affect the equilibrium concentration of ammonia. Some of his results are given in Table 13.2. Note that the equilibrium amount of NH3 increases

TABLE 13.2 The Percent by Mass of NH3 at Equilibrium in a Mixture of N2, H2, and NH3 as a Function of Temperature and Total Pressure*

<i>Temperature (°C)</i>	<i>Total Pressure</i>		
	<i>300 atm</i>	<i>400 atm</i>	<i>500 atm</i>
400	48% <chem>NH3</chem>	55% <chem>NH3</chem>	61% <chem>NH3</chem>
500	26% <chem>NH3</chem>	32% <chem>NH3</chem>	38% <chem>NH3</chem>
600	13% <chem>NH3</chem>	17% <chem>NH3</chem>	21% <chem>NH3</chem>

*Each experiment was begun with a 3:1 mixture of H2 and N2.

with an increase in pressure but decreases as the temperature is increased. Thus the amount of NH₃ present at equilibrium is favored by conditions of low temperature and high pressure.

However, this is not the whole story. Carrying out the process at low temperatures is not feasible because then the reaction is too slow. Even though the equilibrium tends to shift to the right as the temperature is lowered, the attainment of equilibrium would be much too slow at low temperatures to be practical. This emphasizes once again that we must study both the thermodynamics and the kinetics of a reaction before we really understand the factors that control it.

We can qualitatively predict the effects of changes in concentration, pressure, and temperature on a system at equilibrium by using **Le Châtelier's principle**, which states that *if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change*. Although this rule sometimes oversimplifies the situation, it works remarkably well.



Visualization: Le Châtelier's Principle

The Effect of a Change in Concentration

To see how we can predict the effect of change in concentration on a system at equilibrium, we will consider the ammonia synthesis reaction. Suppose there is an equilibrium position described by these concentrations:

$$[\text{N}_2] = 0.399 \text{ M} \quad [\text{H}_2] = 1.197 \text{ M} \quad [\text{NH}_3] = 0.202 \text{ M}$$

What will happen if 1.000 mol/L N₂ is suddenly injected into the system? We can answer this question by calculating the value of *Q*. The concentrations before the system adjusts are

$$\begin{aligned} [\text{N}_2]_0 &= 0.399 \text{ M} + 1.000 \text{ M} = 1.399 \text{ M} \\ &\quad \uparrow \\ &\quad \text{Added N}_2 \\ [\text{H}_2]_0 &= 1.197 \text{ M} \\ [\text{NH}_3]_0 &= 0.202 \text{ M} \end{aligned}$$

Note we are labeling these as “initial concentrations” because the system is no longer at equilibrium. Then

$$Q = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{(0.202)^2}{(1.399)(1.197)^3} = 1.70 \times 10^{-2}$$

Since we are not given the value of *K*, we must calculate it from the first set of equilibrium concentrations:

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.202)^2}{(0.399)(1.197)^3} = 5.96 \times 10^{-2}$$

As expected, *Q* is less than *K* because the concentration of N₂ was increased.

The system will shift to the right to come to the new equilibrium position. Rather than do the calculations, we simply summarize the results:

Equilibrium Position I		Equilibrium Position II
$[\text{N}_2] = 0.399 \text{ M}$ $[\text{H}_2] = 1.197 \text{ M}$ $[\text{NH}_3] = 0.202 \text{ M}$	$\xrightarrow{\text{1.000 mol/L of N}_2 \text{ added}}$	$[\text{N}_2] = 1.348 \text{ M}$ $[\text{H}_2] = 1.044 \text{ M}$ $[\text{NH}_3] = 0.304 \text{ M}$

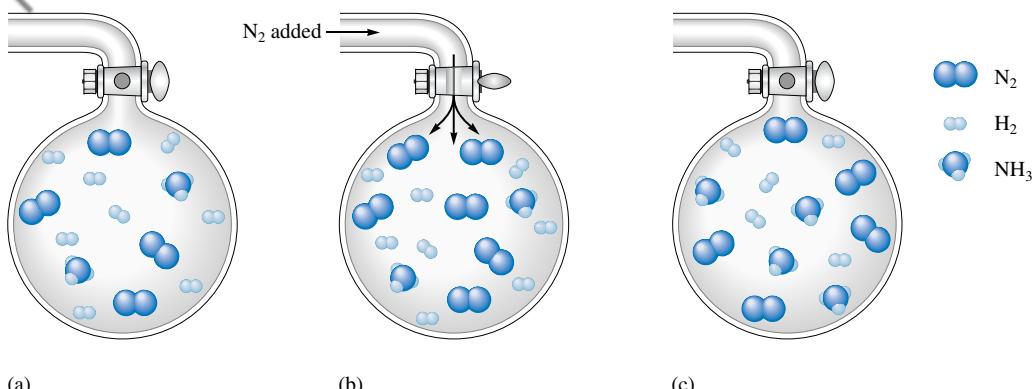


FIGURE 13.8

(a) The initial equilibrium mixture of N_2 , H_2 , and NH_3 . (b) Addition of N_2 . (c) The new equilibrium position for the system containing more N_2 (due to addition of N_2), less H_2 , and more NH_3 than in (a).

Note from these data that the equilibrium position does in fact shift to the right: The concentration of H_2 decreases, the concentration of NH_3 increases, and of course, since nitrogen is added, the concentration of N_2 shows an increase relative to the amount present in the original equilibrium position. (However, notice that the nitrogen showed a decrease relative to the amount present immediately after addition of the 1.000 mol N_2 .)

We can understand this shift by thinking about reaction rates. When we add N₂ molecules to the system, the number of collisions between N₂ and H₂ will increase, thus increasing the rate of the forward reaction and in turn increasing the rate of formation of NH₃ molecules. More NH₃ molecules will in turn lead to a higher rate for the reverse reaction. Eventually, the forward and reverse reaction rates will again become equal, and the system will reach its new equilibrium position.

We can predict this shift qualitatively by using Le Châtelier's principle. Since the change imposed is the addition of nitrogen, Le Châtelier's principle predicts that the system will shift in a direction that consumes nitrogen. This reduces the effect of the addition. Thus Le Châtelier's principle correctly predicts that adding nitrogen will cause the equilibrium to shift to the right (see Fig. 13.8).

If ammonia had been added instead of nitrogen, the system would have shifted to the left to consume ammonia. So another way of stating Le Châtelier's principle is to say that *if a component (reactant or product) is added to a reaction system at equilibrium (at constant T and P or constant T and V), the equilibrium position will shift in the direction that lowers the concentration of that component. If a component is removed, the opposite effect occurs.*

The system shifts in the direction that compensates for the imposed change.

Sample Exercise 13.13

Using Le Châtelier's Principle I

Arsenic can be extracted from its ores by first reacting the ore with oxygen (called *roasting*) to form solid As_4O_6 , which is then reduced using carbon:



Predict the direction of the shift of the equilibrium position in response to each of the following changes in conditions.

- a. Addition of carbon monoxide
 - b. Addition or removal of carbon or tetraarsenic hexoxide (As_4O_6)
 - c. Removal of gaseous arsenic (As_4)

Solution

- a. Le Châtelier's principle predicts that the shift will be away from the substance whose concentration is increased. The equilibrium position will shift to the left when carbon monoxide is added.
 - b. Since the amount of a pure solid has no effect on the equilibrium position, changing the amount of carbon or tetraarsenic hexoxide will have no effect.
 - c. If gaseous arsenic is removed, the equilibrium position will shift to the right to form more products. In industrial processes, the desired product is often continuously removed from the reaction system to increase the yield.

See Exercise 13.57.

The Effect of a Change in Pressure

Basically, there are three ways to change the pressure of a reaction system involving gaseous components:

1. Add or remove a gaseous reactant or product.
 2. Add an inert gas (one not involved in the reaction)
 3. Change the volume of the container.

We have already considered the addition or removal of a reactant or product. When an inert gas is added, there is no effect on the equilibrium position. *The addition of an inert gas increases the total pressure but has no effect on the concentrations or partial pressures of the reactants or products.* That is, in this case the added molecules do not participate in the reaction in any way and thus cannot affect the equilibrium in any way. Thus the system remains at the original equilibrium position.

When the volume of the container is changed, the concentrations (and thus the partial pressures) of both reactants and products are changed. We could calculate Q and predict the direction of the shift. However, for systems involving gaseous components, there is an easier way: We focus on the volume. The central idea is that *when the volume of the*

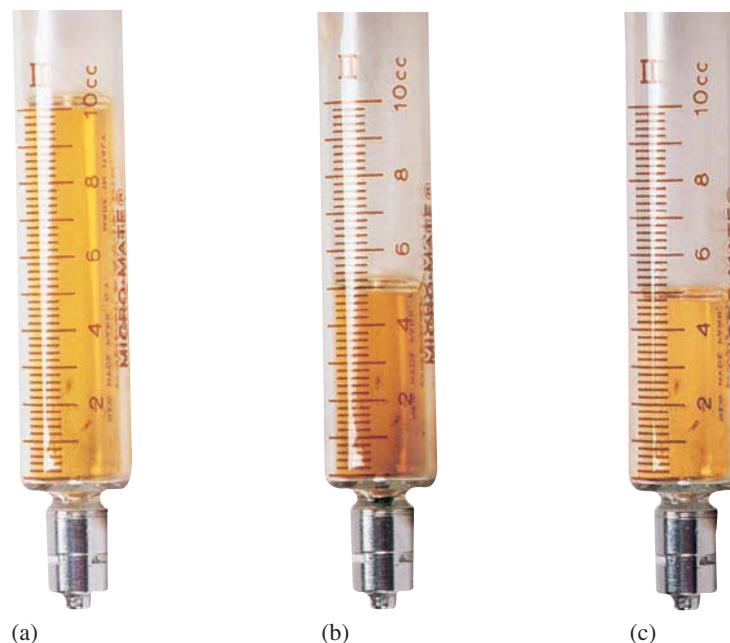
A logo consisting of the letters "www." in blue and orange, positioned above a stylized globe.

Visualization: Equilibrium Decomposition of N_2O_4

(a) Brown $\text{NO}_2(g)$ and colorless $\text{N}_2\text{O}_4(g)$ in equilibrium in a syringe. (b) The volume is suddenly decreased, giving a greater concentration of both N_2O_4 and NO_2 (indicated by the darker brown color). (c) A few seconds after the sudden volume decrease, the color is much lighter brown as the equilibrium shifts the brown $\text{NO}_2(g)$ to colorless $\text{N}_2\text{O}_4(g)$ as predicted by Le Châtelier's principle, since in the equilibrium



the product side has the smaller number of molecules.



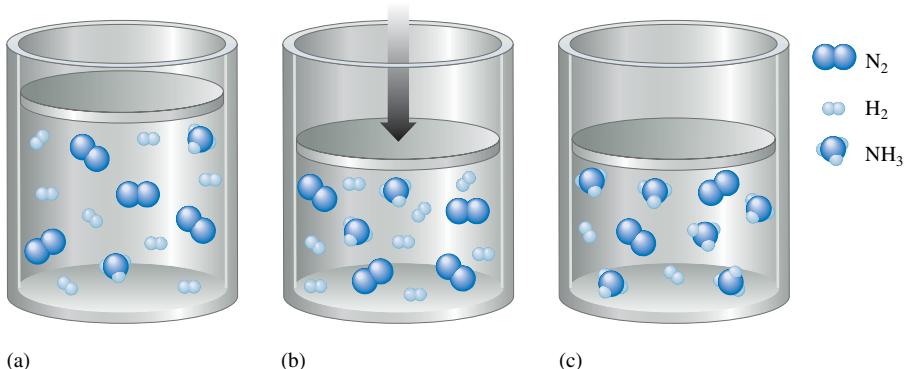


FIGURE 13.9

(a) A mixture of $\text{NH}_3(g)$, $\text{N}_2(g)$, and $\text{H}_2(g)$ at equilibrium. (b) The volume is suddenly decreased. (c) The new equilibrium position for the system containing more NH_3 and less N_2 and H_2 . The reaction $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$ shifts to the right (toward the side with fewer molecules) when the container volume is decreased.

container holding a gaseous system is reduced, the system responds by reducing its own volume. This is done by decreasing the total number of gaseous molecules in the system.

To see that this is true, we can rearrange the ideal gas law to give

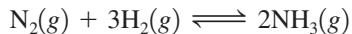
$$V = \left(\frac{RT}{P} \right) n$$

or at constant T and P .

$$V \propto n$$

That is, at constant temperature and pressure, the volume of a gas is directly proportional to the number of moles of gas present.

Suppose we have a mixture of the gases nitrogen, hydrogen, and ammonia at equilibrium (Fig. 13.9). If we suddenly reduce the volume, what will happen to the equilibrium position? The reaction system can reduce its volume by reducing the number of molecules present. This means that the reaction



will shift to the right, since in this direction four molecules (one of nitrogen and three of hydrogen) react to produce two molecules (of ammonia), thus *reducing the total number of gaseous molecules present*. The new equilibrium position will be farther to the right than the original one. That is, the equilibrium position will shift toward the side of the reaction involving the smaller number of gaseous molecules in the balanced equation.

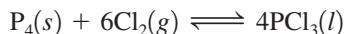
The opposite is also true. When the container volume is increased, the system will shift so as to increase its volume. An increase in volume in the ammonia synthesis system will produce a shift to the left to increase the total number of gaseous molecules present.

Sample Exercise 13.14

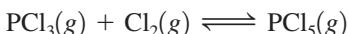
Using Le Châtelier's Principle II

Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced.

- a. The preparation of liquid phosphorus trichloride by the reaction



- b. The preparation of gaseous phosphorus pentachloride according to the equation



- c. The reaction of phosphorus trichloride with ammonia:



Solution

- a. Since P_4 and PCl_3 are a pure solid and a pure liquid, respectively, we need to consider only the effect of the change in volume on Cl_2 . The volume is decreased, so the position

of the equilibrium will shift to the right, since the reactant side contains six gaseous molecules and the product side has none.

- Decreasing the volume will shift the given reaction to the right, since the product side contains only one gaseous molecule while the reactant side has two.
- Both sides of the balanced reaction equation have four gaseous molecules. A change in volume will have no effect on the equilibrium position. There is no shift in this case.

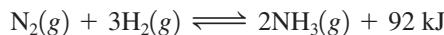
See Exercise 13.58.

The Effect of a Change in Temperature

It is important to realize that although the changes we have just discussed may alter the equilibrium *position*, they do not alter the equilibrium *constant*. For example, the addition of a reactant shifts the equilibrium position to the right but has no effect on the value of the equilibrium constant; the new equilibrium concentrations satisfy the original equilibrium constant.

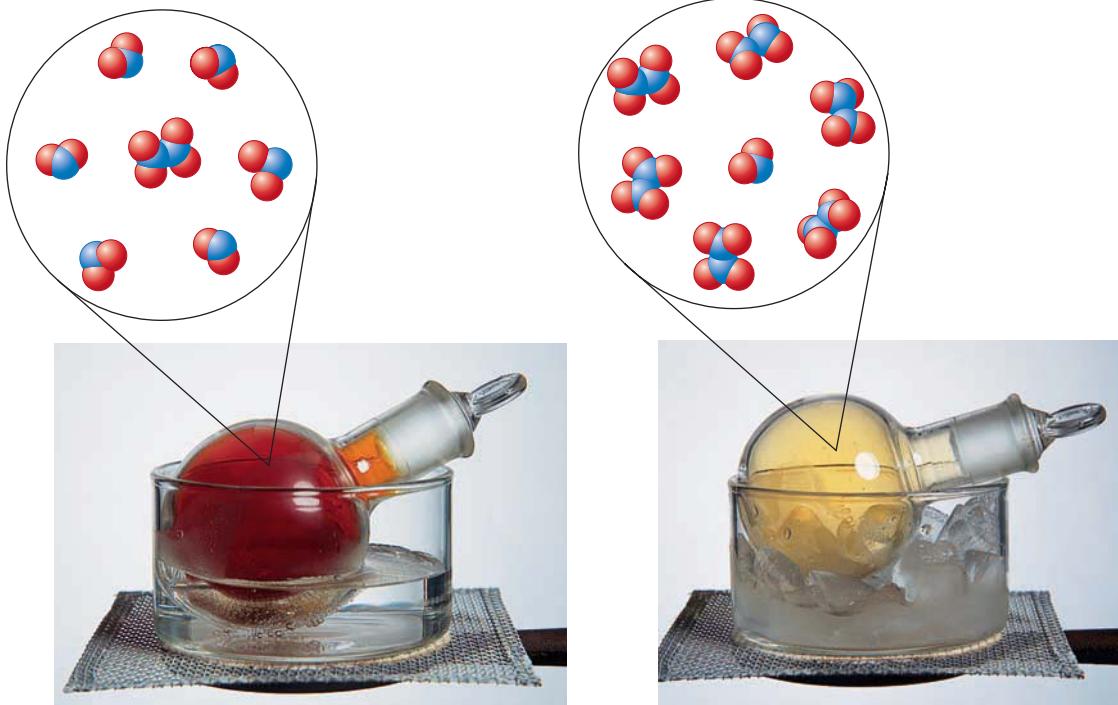
The effect of temperature on equilibrium is different, however, because *the value of K changes with temperature*. We can use Le Châtelier's principle to predict the direction of the change.

The synthesis of ammonia from nitrogen and hydrogen is exothermic. We can represent this by treating energy as a product:



If energy is added to this system at equilibrium by heating it, Le Châtelier's principle predicts that the shift will be in the direction that consumes energy, that is, to the left. Note that this shift decreases the concentration of NH_3 and increases the concentrations of N_2 .

Of course, energy is not a chemical product of this reaction, but thinking of it in this way makes it easy to apply Le Châtelier's principle.



Shifting the $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ equilibrium by changing the temperature. (a) At 100°C the flask is definitely reddish brown due to a large amount of NO_2 present. (b) At 0°C the equilibrium is shifted toward colorless $\text{N}_2\text{O}_4(g)$.

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TABLE 13.3 Observed Value of K for the Ammonia Synthesis Reaction as a Function of Temperature*

Temperature (K)	K
500	90
600	3
700	0.3
800	0.04

*For this exothermic reaction, the value of K decreases as the temperature increases, as predicted by Le Châtelier's principle.

and H_2 , thus *decreasing the value of K* . The experimentally observed change in K with temperature for this reaction is indicated in Table 13.3. The value of K decreases with increased temperature, as predicted.

On the other hand, for an endothermic reaction, such as the decomposition of calcium carbonate,



an increase in temperature will cause the equilibrium to shift to the right and the value of K to increase.

In summary, to use Le Châtelier's principle to describe the effect of a temperature change on a system at equilibrium, treat energy as a reactant (in an endothermic process) or as a product (in an exothermic process), and predict the direction of the shift in the same way as when an actual reactant or product is added or removed. Although Le Châtelier's principle cannot predict the size of the change in K , it does correctly predict the direction of the change.

Sample Exercise 13.15

Using Le Châtelier's Principle III

For each of the following reactions, predict how the value of K changes as the temperature is increased.

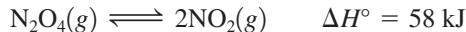
- a. $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \quad \Delta H^\circ = 181 \text{ kJ}$
- b. $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \quad \Delta H^\circ = -198 \text{ kJ}$

Solution

- a. This is an endothermic reaction, as indicated by the positive value for ΔH° . Energy can be viewed as a reactant, and K increases (the equilibrium shifts to the right) as the temperature is increased.
- b. This is an exothermic reaction (energy can be regarded as a product). As the temperature is increased, the value of K decreases (the equilibrium shifts to the left).

See Exercises 13.63 and 13.64.

We have seen how Le Châtelier's principle can be used to predict the effect of several types of changes on a system at equilibrium. To summarize these ideas, Table 13.4 shows how various changes affect the equilibrium position of the endothermic reaction



Key Terms

chemical equilibrium

Section 13.2

law of mass action
equilibrium expression
equilibrium constant
equilibrium position

Section 13.4

homogeneous equilibria
heterogeneous equilibria

Section 13.5

reaction quotient, Q

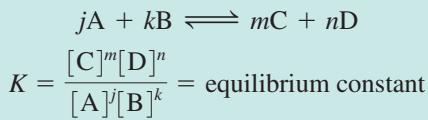
Section 13.7

Le Châtelier's principle

For Review

Chemical equilibrium

- When a reaction takes place in a closed system, it reaches a condition where the concentrations of the reactants and products remain constant over time
- Dynamic state: reactants and products are interconverted continually
 - Forward rate = reverse rate
- The law of mass action: for the reaction



- A pure liquid or solid is never included in the equilibrium expression
- For a gas-phase reaction the reactants and products can be described in terms of their partial pressures and the equilibrium constant is called K_p :

$$K_p = K(RT)^{\Delta n}$$

where Δn is the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants

Equilibrium position

- A set of reactant and product concentrations that satisfies the equilibrium constant expression
- There is one value of K for a given system at a given temperature
- There are an infinite number of equilibrium positions at a given temperature depending on the initial concentrations
- A small value of K means the equilibrium lies to the left; a large value of K means the equilibrium lies to the right
 - The size of K has no relationship to the speed at which equilibrium is achieved
- Q , the reaction quotient, applies the law of mass action to initial concentrations rather than equilibrium concentrations
 - If $Q > K$, the system will shift to the left to achieve equilibrium
 - If $Q < K$, the system will shift to the right to achieve equilibrium
- Finding the concentrations that characterize a given equilibrium position:
 1. Start with the given initial concentrations (pressures)
 2. Define the change needed to reach equilibrium
 3. Apply the change to the initial concentrations (pressures) and solve for the equilibrium concentrations (pressures)

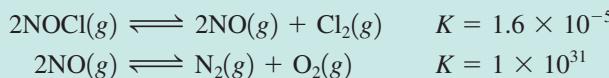
Le Châtelier's principle

- Enables qualitative prediction of the effects of changes in concentration, pressure, and temperature on a system at equilibrium
- If a change in conditions is imposed on a system at equilibrium, the system will shift in a direction that compensates for the imposed change
 - In other words, when a stress is placed on a system at equilibrium, the system shifts in the direction that relieves the stress

REVIEW QUESTIONS

1. Characterize a system at chemical equilibrium with respect to each of the following.
 - a. the rates of the forward and reverse reactions
 - b. the overall composition of the reaction mixture

For a general reaction $3A(g) + B(g) \longrightarrow 2C(g)$, if one starts an experiment with only reactants present, show what the plot of concentrations of A, B, and C versus time would look like. Also sketch the plot illustrating the rate of the forward reaction and rate of the reverse reaction versus time.
2. What is the law of mass action? Is it true that the value of K depends on the amounts of reactants and products mixed together initially? Explain. Is it true that reactions with large equilibrium constant values are very fast? Explain. There is only one value of the equilibrium constant for a particular system at a particular temperature, but there is an infinite number of equilibrium positions. Explain.
3. Consider the following reactions at some temperature:



For each reaction, assume some quantities of the reactants were placed in separate containers and allowed to come to equilibrium. Describe the relative amounts of reactants and products that would be present at equilibrium. At equilibrium, which is faster, the forward or reverse reaction in each case?

4. What is the difference between K and K_p ? When does $K = K_p$ for a reaction? When does $K \neq K_p$ for a reaction? If the coefficients in a reaction equation are tripled, how is the new value of K related to the initial value of K ? If a reaction is reversed, how is the value of K_p for the reversed reaction related to the value of K_p for the initial reaction?
5. What are homogeneous equilibria? Heterogeneous equilibria? What is the difference in writing K expressions for homogeneous versus heterogeneous reactions? Summarize which species are included in the K expression and which species are not included.
6. Distinguish between the terms *equilibrium constant* and *reaction quotient*. When $Q = K$, what does this say about a reaction? When $Q < K$, what does this say about a reaction? When $Q > K$, what does this say about a reaction?
7. Summarize the steps for solving equilibrium problems (see the beginning of Section 13.6). In general, when solving an equilibrium problem, you should always set up an ICE table. What is an ICE table?
8. A common type of reaction we will study is that having a very small K value ($K \ll 1$). Solving for equilibrium concentrations in an equilibrium problem usually requires many mathematical operations to be performed. However, the math involved when solving equilibrium problems for reactions having small K values ($K \ll 1$) is simplified. What assumption is made when solving the equilibrium concentrations for reactions with small K values? Whenever assumptions are made, they must be checked for validity. In general, the “5% rule” is used to check the validity of assuming x (or $2x$, $3x$, and so on) is very small compared to some number. When x (or $2x$, $3x$, and so on) is less than 5% of the number the assumption was made against, then the assumption is said to be valid. If the 5% rule fails, what do you do to solve for the equilibrium concentrations?
9. What is Le Châtelier’s principle? Consider the reaction $2\text{NOCl}(g) \rightleftharpoons 2\text{NO}(g) + \text{Cl}_2(g)$. If this reaction is at equilibrium, what happens when the following changes occur?
 - a. $\text{NOCl}(g)$ is added.
 - b. $\text{NO}(g)$ is added.
 - c. $\text{NOCl}(g)$ is removed.
 - d. $\text{Cl}_2(g)$ is removed.
 - e. The container volume is decreased.For each of these changes, what happens to the value of K for the reaction as equilibrium is reached again? Give an example of a reaction for which the addition or removal of one of the reactants or products has no effect on the equilibrium position.

In general, how will the equilibrium position of a gas-phase reaction be affected if the volume of the reaction vessel changes? Are there reactions that will not have their equilibria shifted by a change in volume? Explain. Why does changing the pressure in a rigid container by adding an inert gas not shift the equilibrium position for a gas-phase reaction?
10. The only “stress” (change) that also changes the value of K is a change in temperature. For an exothermic reaction, how does the equilibrium position change as temperature increases, and what happens to the value of K ? Answer the same questions for an endothermic reaction. If the value of K increases with a decrease in temperature, is the reaction exothermic or endothermic? Explain.

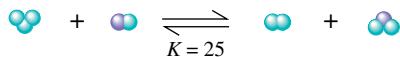
Active Learning Questions

These questions are designed to be used by groups of students in class. The questions allow students to explore their understanding of concepts through discussion and peer teaching. The real value of these questions is the learning that occurs while students talk to each other about chemical concepts.

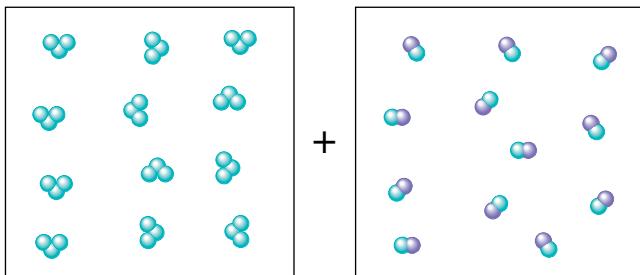
- Consider an equilibrium mixture of four chemicals (A, B, C, and D, all gases) reacting in a closed flask according to the equation:



- You add more A to the flask. How does the concentration of each chemical compare to its original concentration after equilibrium is reestablished? Justify your answer.
- You have the original setup at equilibrium, and add more D to the flask. How does the concentration of each chemical compare to its original concentration after equilibrium is reestablished? Justify your answer.
- The boxes shown below represent a set of initial conditions for the reaction:



Draw a quantitative molecular picture that shows what this system looks like after the reactants are mixed in one of the boxes and the system reaches equilibrium. Support your answer with calculations.



- For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, consider two possibilities: (a) you mix 0.5 mol of each reactant, allow the system to come to equilibrium, and then add another mole of H_2 and allow the system to reach equilibrium again, or (b) you mix 1.5 mol H_2 and 0.5 mol I_2 and allow the system to reach equilibrium. Will the final equilibrium mixture be different for the two procedures? Explain.
- Given the reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$, consider the following situations:
 - You have 1.3 M A and 0.8 M B initially.
 - You have 1.3 M A, 0.8 M B, and 0.2 M C initially.
 - You have 2.0 M A and 0.8 M B initially.

Order the preceding situations in terms of increasing equilibrium concentration of D. Explain your order. Then give the

order in terms of increasing equilibrium concentration of B and explain.

- Consider the reaction $A(g) + 2B(g) \rightleftharpoons C(g) + D(g)$ in a 1.0-L rigid flask. Answer the following questions for each situation (a–d):
 - Estimate a range (as small as possible) for the requested substance. For example, [A] could be between 95 M and 100 M.
 - Explain how you decided on the limits for the estimated range.
 - Indicate what other information would enable you to narrow your estimated range.
 - Compare the estimated concentrations for a through d, and explain any differences.
- If at equilibrium $[A] = 1\text{ M}$, and then 1 mol C is added, estimate the value for [A] once equilibrium is reestablished.
- If at equilibrium $[B] = 1\text{ M}$, and then 1 mol C is added, estimate the value for [B] once equilibrium is reestablished.
- If at equilibrium $[C] = 1\text{ M}$, and then 1 mol C is added, estimate the value for [C] once equilibrium is reestablished.
- If at equilibrium $[D] = 1\text{ M}$, and then 1 mol C is added, estimate the value for [D] once equilibrium is reestablished.
- Consider the reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$. A friend asks the following: “I know we have been told that if a mixture of A, B, C, and D is at equilibrium and more of A is added, more C and D will form. But how can more C and D form if we do not add more B?” What do you tell your friend?
- Consider the following statements: “Consider the reaction $A(g) + B(g) \rightleftharpoons C(g)$, for which at equilibrium $[A] = 2\text{ M}$, $[B] = 1\text{ M}$, and $[C] = 4\text{ M}$. To a 1-L container of the system at equilibrium you add 3 moles of B. A possible equilibrium condition is $[A] = 1\text{ M}$, $[B] = 3\text{ M}$, and $[C] = 6\text{ M}$ because in both cases $K = 2$.” Indicate everything that is correct in these statements and everything that is incorrect. Correct the incorrect statements, and explain.
- Le Châtelier’s principle is stated (Section 13.7) as follows: “If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.” The system $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is used as an example in which the addition of nitrogen gas at equilibrium results in a decrease in H_2 concentration and an increase in NH_3 concentration. In the experiment the volume is assumed to be constant. On the other hand, if N_2 is added to the reaction system in a container with a piston so that the pressure can be held constant, the amount of NH_3 actually could decrease and the concentration of H_2 would increase as equilibrium is reestablished. Explain how this can happen. Also, if you consider this same system at equilibrium, the addition of an inert gas, holding the pressure constant, does affect the equilibrium position. Explain why the addition of an inert gas to this system in a rigid container does not affect the equilibrium position.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

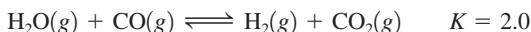
9. Consider the following reaction:



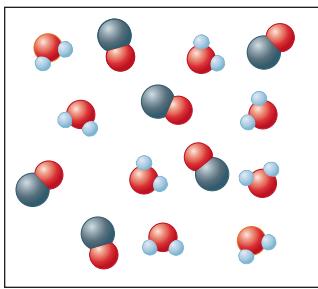
Amounts of H_2O , CO , H_2 , and CO_2 are put into a flask so that the composition corresponds to an equilibrium position. If the CO placed in the flask is labeled with radioactive ^{14}C , will ^{14}C be found only in CO molecules for an indefinite period of time? Explain.

10. Consider the same reaction as in Exercise 9. In one experiment 1.0 mol $\text{H}_2\text{O}(g)$ and 1.0 mol $\text{CO}(g)$ are put into a flask and heated to 350°C . In a second experiment 1.0 mol $\text{H}_2(g)$ and 1.0 mol $\text{CO}_2(g)$ are put into another flask with the same volume as the first. This mixture is also heated to 350°C . After equilibrium is reached, will there be any difference in the composition of the mixtures in the two flasks?

11. Consider the following reaction at some temperature:

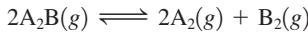


Some molecules of H_2O and CO are placed in a 1.0-L container as shown below.

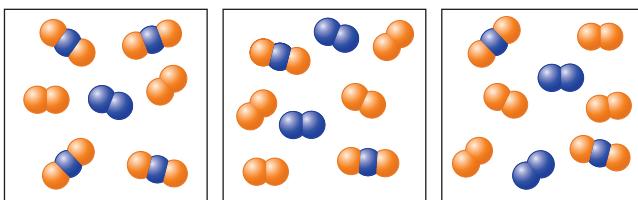


When equilibrium is reached, how many molecules of H_2O , CO , H_2 and CO_2 are present? Do this problem by trial and error—that is, if two molecules of CO react, is this equilibrium; if three molecules of CO react, is this equilibrium; and so on.

12. Consider the following generic reaction:



Some molecules of A_2B are placed in a 1.0-L container. As time passes, several snapshots of the reaction mixture are taken as illustrated below.



Which illustration is the first to represent an equilibrium mixture? Explain. How many molecules of A_2B reacted initially?

13. Explain the difference between K , K_p , and Q .

14. Consider the following reactions.



List two property differences between these two reactions that relate to equilibrium.

15. For a typical equilibrium problem, the value of K and the initial reaction conditions are given for a specific reaction, and you are asked to calculate the equilibrium concentrations. Many of these calculations involve solving a quadratic or cubic equation. What can you do to avoid solving a quadratic or cubic equation and still come up with reasonable equilibrium concentrations?

16. Which of the following statements is(are) true? Correct the false statement(s).

- a. When a reactant is added to a system at equilibrium at a given temperature, the reaction will shift right to reestablish equilibrium.
- b. When a product is added to a system at equilibrium at a given temperature, the value of K for the reaction will increase when equilibrium is reestablished.
- c. When temperature is increased for a reaction at equilibrium, the value of K for the reaction will increase.
- d. When the volume of a reaction container is increased for a system at equilibrium at a given temperature, the reaction will shift left to reestablish equilibrium.
- e. Addition of a catalyst (a substance that increases the speed of the reaction) has no effect on the equilibrium position.

Exercises

In this section similar exercises are paired.

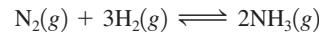
The Equilibrium Constant

17. Write the equilibrium expression (K) for each of the following gas-phase reactions.

- a. $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$
- b. $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$
- c. $\text{SiH}_4(g) + 2\text{Cl}_2(g) \rightleftharpoons \text{SiCl}_4(g) + 2\text{H}_2(g)$
- d. $2\text{PBr}_3(g) + 3\text{Cl}_2(g) \rightleftharpoons 2\text{PCl}_3(g) + 3\text{Br}_2(g)$

18. Write the equilibrium expression (K_p) for each reaction in Exercise 17.

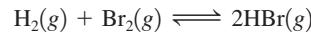
19. At a given temperature, $K = 1.3 \times 10^{-2}$ for the reaction



Calculate values of K for the following reactions at this temperature.

- a. $\frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g) \rightleftharpoons \text{NH}_3(g)$
- b. $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$
- c. $\text{NH}_3(g) \rightleftharpoons \frac{1}{2}\text{N}_2(g) + \frac{3}{2}\text{H}_2(g)$
- d. $2\text{N}_2(g) + 6\text{H}_2(g) \rightleftharpoons 4\text{NH}_3(g)$

20. For the reaction



$K_p = 3.5 \times 10^4$ at 1495 K . What is the value of K_p for the following reactions at 1495 K ?

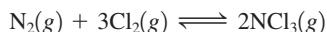
- a. $\text{HBr}(g) \rightleftharpoons \frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{Br}_2(g)$
- b. $2\text{HBr}(g) \rightleftharpoons \text{H}_2(g) + \text{Br}_2(g)$
- c. $\frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{Br}_2(g) \rightleftharpoons \text{HBr}(g)$

21. For the reaction



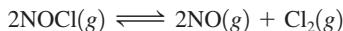
it is determined that, at equilibrium at a particular temperature, the concentrations are as follows: $[\text{NO}(g)] = 8.1 \times 10^{-3} M$, $[\text{H}_2(g)] = 4.1 \times 10^{-5} M$, $[\text{N}_2(g)] = 5.3 \times 10^{-2} M$, and $[\text{H}_2\text{O}(g)] = 2.9 \times 10^{-3} M$. Calculate the value of K for the reaction at this temperature.

22. For the reaction

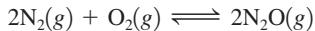


an analysis of an equilibrium mixture is performed at a certain temperature. It is found that $[\text{NCl}_3(g)] = 1.9 \times 10^{-1} M$, $[\text{N}_2(g)] = 1.4 \times 10^{-3} M$, and $[\text{Cl}_2(g)] = 4.3 \times 10^{-4} M$. Calculate K for the reaction at this temperature.

23. At a particular temperature, a 3.0-L flask contains 2.4 mol Cl_2 , 1.0 mol NOCl , and 4.5×10^{-3} mol NO. Calculate K at this temperature for the following reaction:

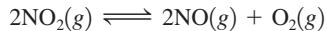


24. At a particular temperature a 2.00-L flask at equilibrium contains 2.80×10^{-4} mol N_2 , 2.50×10^{-5} mol O_2 , and 2.00×10^{-2} mol N_2O . Calculate K at this temperature for the reaction



If $[\text{N}_2] = 2.00 \times 10^{-4} M$, $[\text{N}_2\text{O}] = 0.200 M$, and $[\text{O}_2] = 0.00245 M$, does this represent a system at equilibrium?

25. The following equilibrium pressures at a certain temperature were observed for the reaction



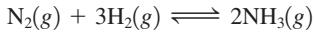
$$P_{\text{NO}_2} = 0.55 \text{ atm}$$

$$P_{\text{NO}} = 6.5 \times 10^{-5} \text{ atm}$$

$$P_{\text{O}_2} = 4.5 \times 10^{-5} \text{ atm}$$

Calculate the value for the equilibrium constant K_p at this temperature.

26. The following equilibrium pressures were observed at a certain temperature for the reaction



$$P_{\text{NH}_3} = 3.1 \times 10^{-2} \text{ atm}$$

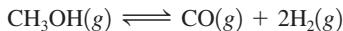
$$P_{\text{N}_2} = 8.5 \times 10^{-1} \text{ atm}$$

$$P_{\text{H}_2} = 3.1 \times 10^{-3} \text{ atm}$$

Calculate the value for the equilibrium constant K_p at this temperature.

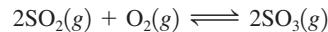
If $P_{\text{N}_2} = 0.525 \text{ atm}$, $P_{\text{NH}_3} = 0.0167 \text{ atm}$, and $P_{\text{H}_2} = 0.00761 \text{ atm}$, does this represent a system at equilibrium?

27. At 327°C , the equilibrium concentrations are $[\text{CH}_3\text{OH}] = 0.15 M$, $[\text{CO}] = 0.24 M$, and $[\text{H}_2] = 1.1 M$ for the reaction



Calculate K_p at this temperature.

28. At 1100 K , $K_p = 0.25$ for the reaction



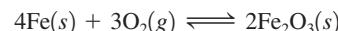
What is the value of K at this temperature?

29. Write expressions for K and K_p for the following reactions.

- a. $2\text{NH}_3(g) + \text{CO}_2(g) \rightleftharpoons \text{N}_2\text{CH}_4\text{O}(s) + \text{H}_2\text{O}(g)$
- b. $2\text{NBr}_3(s) \rightleftharpoons \text{N}_2(g) + 3\text{Br}_2(g)$
- c. $2\text{KClO}_3(s) \rightleftharpoons 2\text{KCl}(s) + 3\text{O}_2(g)$
- d. $\text{CuO}(s) + \text{H}_2(g) \rightleftharpoons \text{Cu}(l) + \text{H}_2\text{O}(g)$

30. For which reactions in Exercise 29 is K_p equal to K ?

31. Consider the following reaction at a certain temperature:



An equilibrium mixture contains 1.0 mol Fe, 1.0×10^{-3} mol O_2 , and 2.0 mol Fe_2O_3 all in a 2.0-L container. Calculate the value of K for this reaction.

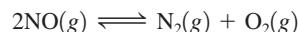
32. In a study of the reaction



at 1200 K it was observed that when the equilibrium partial pressure of water vapor is 15.0 torr, that total pressure at equilibrium is 36.3 torr. Calculate the value of K_p for this reaction at 1200 K . Hint: Apply Dalton's law of partial pressures.

Equilibrium Calculations

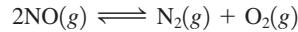
33. The equilibrium constant, K , is 2.4×10^3 at a certain temperature for the reaction



For which of the following sets of conditions is the system at equilibrium? For those that are not at equilibrium, in which direction will the system shift?

- a. A 1.0-L flask contains 0.024 mol NO, 2.0 mol N_2 , and 2.6 mol O_2 .
- b. A 2.0-L flask contains 0.032 mol NO, 0.62 mol N_2 , and 4.0 mol O_2 .
- c. A 3.0-L flask contains 0.060 mol NO, 2.4 mol N_2 , and 1.7 mol O_2 .

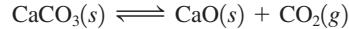
34. The equilibrium constant, K_p , is 2.4×10^3 at a certain temperature for the reaction



For which of the following sets of conditions is the system at equilibrium? For those that are not at equilibrium, in which direction will the system shift?

- a. $P_{\text{NO}} = 0.010 \text{ atm}$, $P_{\text{N}_2} = 0.11 \text{ atm}$, $P_{\text{O}_2} = 2.0 \text{ atm}$
- b. $P_{\text{NO}} = 0.0078 \text{ atm}$, $P_{\text{N}_2} = 0.36 \text{ atm}$, $P_{\text{O}_2} = 0.67 \text{ atm}$
- c. $P_{\text{NO}} = 0.0062 \text{ atm}$, $P_{\text{N}_2} = 0.51 \text{ atm}$, $P_{\text{O}_2} = 0.18 \text{ atm}$

35. At 900°C , $K_p = 1.04$ for the reaction



At a low temperature, dry ice (solid CO_2), calcium oxide, and calcium carbonate are introduced into a 50.0-L reaction chamber. The temperature is raised to 900°C , resulting in the dry ice

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converting to gaseous CO_2 . For the following mixtures, will the initial amount of calcium oxide increase, decrease, or remain the same as the system moves toward equilibrium at 900°C ?

- 655 g CaCO_3 , 95.0 g CaO , $P_{\text{CO}_2} = 2.55 \text{ atm}$
- 780 g CaCO_3 , 1.00 g CaO , $P_{\text{CO}_2} = 1.04 \text{ atm}$
- 0.14 g CaCO_3 , 5000 g CaO , $P_{\text{CO}_2} = 1.04 \text{ atm}$
- 715 g CaCO_3 , 813 g CaO , $P_{\text{CO}_2} = 0.211 \text{ atm}$

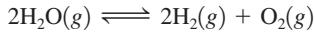
- 36.** Ethyl acetate is synthesized in a nonreacting solvent (not water) according to the following reaction:



For the following mixtures (a–d), will the concentration of H_2O increase, decrease, or remain the same as equilibrium is established?

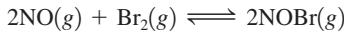
- $[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] = 0.22 \text{ M}$, $[\text{H}_2\text{O}] = 0.10 \text{ M}$, $[\text{CH}_3\text{CO}_2\text{H}] = 0.010 \text{ M}$, $[\text{C}_2\text{H}_5\text{OH}] = 0.010 \text{ M}$
- $[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] = 0.22 \text{ M}$, $[\text{H}_2\text{O}] = 0.0020 \text{ M}$, $[\text{CH}_3\text{CO}_2\text{H}] = 0.0020 \text{ M}$, $[\text{C}_2\text{H}_5\text{OH}] = 0.10 \text{ M}$
- $[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] = 0.88 \text{ M}$, $[\text{H}_2\text{O}] = 0.12 \text{ M}$, $[\text{CH}_3\text{CO}_2\text{H}] = 0.044 \text{ M}$, $[\text{C}_2\text{H}_5\text{OH}] = 6.0 \text{ M}$
- $[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] = 4.4 \text{ M}$, $[\text{H}_2\text{O}] = 4.4 \text{ M}$, $[\text{CH}_3\text{CO}_2\text{H}] = 0.88 \text{ M}$, $[\text{C}_2\text{H}_5\text{OH}] = 10.0 \text{ M}$
- What must the concentration of water be for a mixture with $[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] = 2.0 \text{ M}$, $[\text{CH}_3\text{CO}_2\text{H}] = 0.10 \text{ M}$, $[\text{C}_2\text{H}_5\text{OH}] = 5.0 \text{ M}$ to be at equilibrium?
- Why is water included in the equilibrium expression for this reaction?

- 37.** For the reaction



$K = 2.4 \times 10^{-3}$ at a given temperature. At equilibrium it is found that $[\text{H}_2\text{O}(g)] = 1.1 \times 10^{-1} \text{ M}$ and $[\text{H}_2(g)] = 1.9 \times 10^{-2} \text{ M}$. What is the concentration of $\text{O}_2(g)$ under these conditions?

- 38.** The reaction



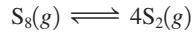
has $K_p = 109$ at 25°C . If the equilibrium partial pressure of Br_2 is 0.0159 atm and the equilibrium partial pressure of NOBr is 0.0768 atm, calculate the partial pressure of NO at equilibrium.

- 39.** A 1.00-L flask was filled with 2.00 mol gaseous SO_2 and 2.00 mol gaseous NO_2 and heated. After equilibrium was reached, it was found that 1.30 mol gaseous NO was present. Assume that the reaction



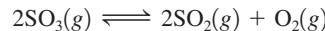
occurs under these conditions. Calculate the value of the equilibrium constant, K , for this reaction.

- 40.** A sample of $\text{S}_8(g)$ is placed in an otherwise empty rigid container at 1325 K at an initial pressure of 1.00 atm, where it decomposes to $\text{S}_2(g)$ by the reaction



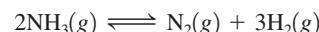
At equilibrium, the partial pressure of S_8 is 0.25 atm. Calculate K_p for this reaction at 1325 K .

- 41.** At a particular temperature, 12.0 mol of SO_3 is placed into a 3.0-L rigid container, and the SO_3 dissociates by the reaction



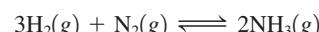
At equilibrium, 3.0 mol of SO_2 is present. Calculate K for this reaction.

- 42.** At a certain temperature, 4.0 mol NH_3 is introduced into a 2.0-L container, and the NH_3 partially dissociates by the reaction



At equilibrium, 2.0 mol NH_3 remains. What is the value of K for this reaction?

- 43.** An initial mixture of nitrogen gas and hydrogen gas is reacted in a rigid container at a certain temperature by the reaction



At equilibrium, the concentrations are $[\text{H}_2] = 5.0 \text{ M}$, $[\text{N}_2] = 8.0 \text{ M}$, and $[\text{NH}_3] = 4.0 \text{ M}$. What were the concentrations of nitrogen gas and hydrogen gas that were reacted initially?

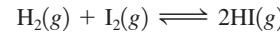
- 44.** Nitrogen gas (N_2) reacts with hydrogen gas (H_2) to form ammonia (NH_3). At 200°C in a closed container, 1.00 atm of nitrogen gas is mixed with 2.00 atm of hydrogen gas. At equilibrium, the total pressure is 2.00 atm. Calculate the partial pressure of hydrogen gas at equilibrium.

- 45.** At a particular temperature, $K = 3.75$ for the reaction



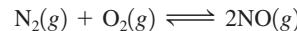
If all four gases had initial concentrations of 0.800 M , calculate the equilibrium concentrations of the gases.

- 46.** At a particular temperature, $K = 1.00 \times 10^2$ for the reaction



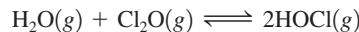
In an experiment, 1.00 mol H_2 , 1.00 mol I_2 , and 1.00 mol HI are introduced into a 1.00-L container. Calculate the concentrations of all species when equilibrium is reached.

- 47.** At 2200°C , $K_p = 0.050$ for the reaction



What is the partial pressure of NO in equilibrium with N_2 and O_2 that were placed in a flask at initial pressures of 0.80 and 0.20 atm, respectively?

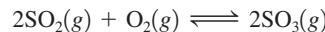
- 48.** At 25°C , $K = 0.090$ for the reaction



Calculate the concentrations of all species at equilibrium for each of the following cases.

- 1.0 g H_2O and 2.0 g Cl_2O are mixed in a 1.0-L flask.
- 1.0 mol pure HOCl is placed in a 2.0-L flask.

- 49.** At 1100 K , $K_p = 0.25$ for the reaction



Calculate the equilibrium partial pressures of SO_2 , O_2 , and SO_3 produced from an initial mixture in which $P_{\text{SO}_2} = P_{\text{O}_2} = 0.50 \text{ atm}$ and $P_{\text{SO}_3} = 0$. (Hint: If you don't have a graphing calculator, then

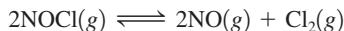
use the method of successive approximations to solve, as discussed in Appendix 1.4.)

50. At a particular temperature, $K_p = 0.25$ for the reaction



- a. A flask containing only N_2O_4 at an initial pressure of 4.5 atm is allowed to reach equilibrium. Calculate the equilibrium partial pressures of the gases.
- b. A flask containing only NO_2 at an initial pressure of 9.0 atm is allowed to reach equilibrium. Calculate the equilibrium partial pressures of the gases.
- c. From your answers to parts a and b, does it matter from which direction an equilibrium position is reached?

51. At 35°C , $K = 1.6 \times 10^{-5}$ for the reaction



Calculate the concentrations of all species at equilibrium for each of the following original mixtures.

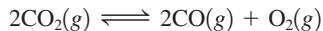
- a. 2.0 mol pure NOCl in a 2.0-L flask
- b. 1.0 mol NOCl and 1.0 mol NO in a 1.0-L flask
- c. 2.0 mol NOCl and 1.0 mol Cl_2 in a 1.0-L flask

52. At a particular temperature, $K = 4.0 \times 10^{-7}$ for the reaction



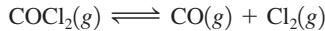
In an experiment, 1.0 mol N_2O_4 is placed in a 10.0-L vessel. Calculate the concentrations of N_2O_4 and NO_2 when this reaction reaches equilibrium.

53. At a particular temperature, $K = 2.0 \times 10^{-6}$ for the reaction



If 2.0 mol CO_2 is initially placed into a 5.0-L vessel, calculate the equilibrium concentrations of all species.

54. Lexan is a plastic used to make compact discs, eyeglass lenses, and bullet-proof glass. One of the compounds used to make Lexan is phosgene (COCl_2), an extremely poisonous gas. Phosgene decomposes by the reaction



for which $K_p = 6.8 \times 10^{-9}$ at 100°C . If pure phosgene at an initial pressure of 1.0 atm decomposes, calculate the equilibrium pressures of all species.

55. At 25°C , $K_p = 2.9 \times 10^{-3}$ for the reaction



In an experiment carried out at 25°C , a certain amount of $\text{NH}_4\text{OCONH}_2$ is placed in an evacuated rigid container and allowed to come to equilibrium. Calculate the total pressure in the container at equilibrium.

56. A sample of solid ammonium chloride was placed in an evacuated container and then heated so that it decomposed to ammonia gas and hydrogen chloride gas. After heating, the total pressure in the container was found to be 4.4 atm. Calculate K_p at this temperature for the decomposition reaction



Le Châtelier's Principle

57. Suppose the reaction system



has already reached equilibrium. Predict the effect that each of the following changes will have on the equilibrium position. Tell whether the equilibrium will shift to the right, will shift to the left, or will not be affected.

- a. Additional $\text{UO}_2(s)$ is added to the system.
- b. The reaction is performed in a glass reaction vessel; $\text{HF}(g)$ attacks and reacts with glass.
- c. Water vapor is removed.

58. Predict the shift in the equilibrium position that will occur for each of the following reactions when the volume of the reaction container is increased.

- a. $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$
- b. $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$
- c. $\text{H}_2(g) + \text{F}_2(g) \rightleftharpoons 2\text{HF}(g)$
- d. $\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$
- e. $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$

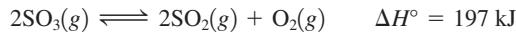
59. An important reaction in the commercial production of hydrogen is



How will this system at equilibrium shift in each of the five following cases?

- a. Gaseous carbon dioxide is removed.
- b. Water vapor is added.
- c. The pressure is increased by adding helium gas.
- d. The temperature is increased (the reaction is exothermic).
- e. The pressure is increased by decreasing the volume of the reaction container.

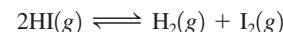
60. What will happen to the number of moles of SO_3 in equilibrium with SO_2 and O_2 in the reaction



in each of the following cases?

- a. Oxygen gas is added.
- b. The pressure is increased by decreasing the volume of the reaction container.
- c. The pressure is increased by adding argon gas.
- d. The temperature is decreased.
- e. Gaseous sulfur dioxide is removed.

61. In which direction will the position of the equilibrium



be shifted for each of the following changes?

- a. $\text{H}_2(g)$ is added.
- b. $\text{I}_2(g)$ is removed.
- c. $\text{HI}(g)$ is removed.
- d. Some $\text{Ar}(g)$ is added.
- e. The volume of the container is doubled.
- f. The temperature is decreased (the reaction is exothermic).

62. Hydrogen for use in ammonia production is produced by the reaction



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What will happen to a reaction mixture at equilibrium if

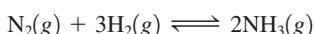
- $\text{H}_2\text{O}(g)$ is removed?
- the temperature is increased (the reaction is endothermic)?
- an inert gas is added?
- $\text{CO}(g)$ is removed?
- the volume of the container is tripled?

63. Old-fashioned “smelling salts” consist of ammonium carbonate, $(\text{NH}_4)_2\text{CO}_3$. The reaction for the decomposition of ammonium carbonate



is endothermic. Would the smell of ammonia increase or decrease as the temperature is increased?

64. Ammonia is produced by the Haber process, in which nitrogen and hydrogen are reacted directly using an iron mesh impregnated with oxides as a catalyst. For the reaction



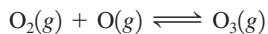
equilibrium constants (K_p values) as a function of temperature are

300°C,	4.34×10^{-3}
500°C,	1.45×10^{-5}
600°C,	2.25×10^{-6}

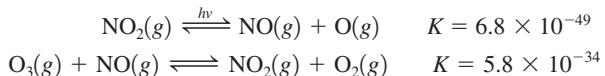
Is the reaction exothermic or endothermic?

Additional Exercises

65. Calculate a value for the equilibrium constant for the reaction

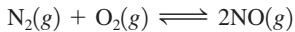


given



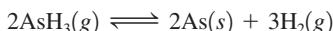
Hint: When reactions are added together, the equilibrium expressions are multiplied.

66. At 25°C, $K_p \approx 1 \times 10^{-31}$ for the reaction



- Calculate the concentration of NO, in molecules/cm³, that can exist in equilibrium in air at 25°C. In air, $P_{\text{N}_2} = 0.8$ atm and $P_{\text{O}_2} = 0.2$ atm.
- Typical concentrations of NO in relatively pristine environments range from 10^8 to 10^{10} molecules/cm³. Why is there a discrepancy between these values and your answer to part a?

67. The gas arsine, AsH_3 , decomposes as follows:



In an experiment at a certain temperature, pure $\text{AsH}_3(g)$ was placed in an empty, rigid, sealed flask at a pressure of 392.0 torr. After 48 hours the pressure in the flask was observed to be constant at 488.0 torr.

- Calculate the equilibrium pressure of $\text{H}_2(g)$
- Calculate K_p for this reaction.

68. At a certain temperature, $K = 9.1 \times 10^{-4}$ for the reaction



Calculate the concentrations of Fe^{3+} , SCN^- , and FeSCN^{2+} in a solution that is initially 2.0 M FeSCN^{2+} .

69. For the reaction

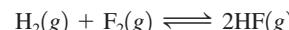


at 600. K, the equilibrium constant, K_p , is 11.5. Suppose that 2.450 g of PCl_5 is placed in an evacuated 500.-mL bulb, which is then heated to 600. K.

- What would be the pressure of PCl_5 if it did not dissociate?
- What is the partial pressure of PCl_5 at equilibrium?
- What is the total pressure in the bulb at equilibrium?
- What is the degree of dissociation of PCl_5 at equilibrium?

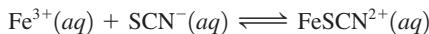
70. At 25°C, gaseous SO_2Cl_2 decomposes to $\text{SO}_2(g)$ and $\text{Cl}_2(g)$ to the extent that 12.5% of the original SO_2Cl_2 (by moles) has decomposed to reach equilibrium. The total pressure (at equilibrium) is 0.900 atm. Calculate the value of K_p for this system.

71. For the following reaction at a certain temperature



it is found that the equilibrium concentrations in a 5.00-L rigid container are $[\text{H}_2] = 0.0500$ M, $[\text{F}_2] = 0.0100$ M, and $[\text{HF}] = 0.400$ M. If 0.200 mol of F_2 is added to this equilibrium mixture, calculate the concentrations of all gases once equilibrium is reestablished.

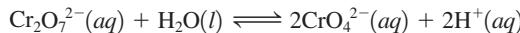
72. Consider the reaction



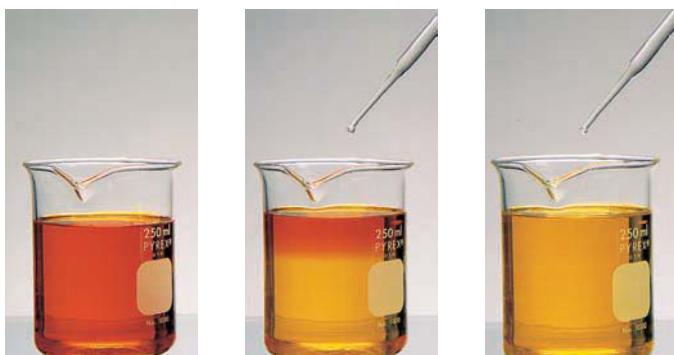
How will the equilibrium position shift if

- water is added, doubling the volume?
- $\text{AgNO}_3(aq)$ is added? (AgSCN is insoluble.)
- $\text{NaOH}(aq)$ is added? (Fe(OH)_3 is insoluble.)
- $\text{Fe}(\text{NO}_3)_3(aq)$ is added?

73. Chromium(VI) forms two different oxyanions, the orange dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$, and the yellow chromate ion, CrO_4^{2-} . (See the following photos.) The equilibrium reaction between the two ions is



Explain why orange dichromate solutions turn yellow when sodium hydroxide is added.



74. The synthesis of ammonia gas from nitrogen gas and hydrogen gas represents a classic case in which a knowledge of kinetics and equilibrium was used to make a desired chemical reaction economically feasible. Explain how each of the following conditions helps to maximize the yield of ammonia.

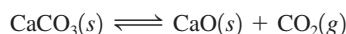
- running the reaction at an elevated temperature
- removing the ammonia from the reaction mixture as it forms
- using a catalyst
- running the reaction at high pressure

75. Suppose $K = 4.5 \times 10^{-3}$ at a certain temperature for the reaction



If it is found that the concentration of PCl_5 is twice the concentration of PCl_3 , what must be the concentration of Cl_2 under these conditions?

76. For the reaction below, $K_p = 1.16$ at 800°C .



If a 20.0-g sample of CaCO_3 is put into a 10.0-L container and heated to 800°C , what percentage by mass of the CaCO_3 will react to reach equilibrium?

77. A 2.4156-g sample of PCl_5 was placed in an empty 2.000-L flask and allowed to decompose to PCl_3 and Cl_2 at 250.0°C :



At equilibrium the total pressure inside the flask was observed to be 358.7 torr. Calculate the partial pressure of each gas at equilibrium and the value of K_p at 250.0°C .

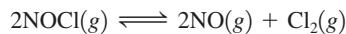
78. Consider the decomposition of the compound $\text{C}_5\text{H}_6\text{O}_3$ as follows:



When a 5.63-g sample of pure $\text{C}_5\text{H}_6\text{O}_3(g)$ was sealed into an otherwise empty 2.50-L flask and heated to 200°C , the pressure in the flask gradually rose to 1.63 atm and remained at that value. Calculate K for this reaction.

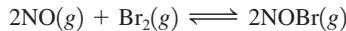
Challenge Problems

79. At 35°C , $K = 1.6 \times 10^{-5}$ for the reaction



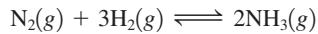
If 2.0 mol NO and 1.0 mol Cl_2 are placed into a 1.0-L flask, calculate the equilibrium concentrations of all species.

80. Nitric oxide and bromine at initial partial pressures of 98.4 and 41.3 torr, respectively, were allowed to react at 300°K . At equilibrium the total pressure was 110.5 torr. The reaction is



- Calculate the value of K_p .
- What would be the partial pressures of all species if NO and Br_2 , both at an initial partial pressure of 0.30 atm, were allowed to come to equilibrium at this temperature?

81. At 25°C , $K_p = 5.3 \times 10^5$ for the reaction



When a certain partial pressure of $\text{NH}_3(g)$ is put into an otherwise empty rigid vessel at 25°C , equilibrium is reached when

50.0% of the original ammonia has decomposed. What was the original partial pressure of ammonia before any decomposition occurred?

82. Consider the reaction



where $K_p = 1.00 \times 10^{-1}$ at 1325°K . In an experiment where $\text{P}_4(g)$ is placed into a container at 1325°K , the equilibrium mixture of $\text{P}_4(g)$ and $\text{P}_2(g)$ has a total pressure of 1.00 atm. Calculate the equilibrium pressures of $\text{P}_4(g)$ and $\text{P}_2(g)$. Calculate the fraction (by moles) of $\text{P}_4(g)$ that has dissociated to reach equilibrium.

83. The partial pressures of an equilibrium mixture of $\text{N}_2\text{O}_4(g)$ and $\text{NO}_2(g)$ are $P_{\text{N}_2\text{O}_4} = 0.34$ atm and $P_{\text{NO}_2} = 1.20$ atm at a certain temperature. The volume of the container is doubled. Find the partial pressures of the two gases when a new equilibrium is established.

84. At 125°C , $K_p = 0.25$ for the reaction



A 1.00-L flask containing 10.0 g NaHCO_3 is evacuated and heated to 125°C .

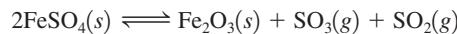
- Calculate the partial pressures of CO_2 and H_2O after equilibrium is established.
- Calculate the masses of NaHCO_3 and Na_2CO_3 present at equilibrium.
- Calculate the minimum container volume necessary for all of the NaHCO_3 to decompose.

85. An 8.00-g sample of SO_3 was placed in an evacuated container, where it decomposed at 600°C according to the following reaction:



At equilibrium the total pressure and the density of the gaseous mixture were 1.80 atm and 1.60 g/L, respectively. Calculate K_p for this reaction.

86. A sample of iron(II) sulfate was heated in an evacuated container to 920°K , where the following reactions occurred:



After equilibrium was reached, the total pressure was 0.836 atm and the partial pressure of oxygen was 0.0275 atm. Calculate K_p for each of these reactions.

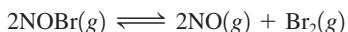
87. At 5000°K and 1.000 atm, 83.00% of the oxygen molecules in a sample have dissociated to atomic oxygen. At what pressure will 95.0% of the molecules dissociate at this temperature?

88. A sample of $\text{N}_2\text{O}_4(g)$ is placed in an empty cylinder at 25°C . After equilibrium is reached the total pressure is 1.5 atm and 16% (by moles) of the original $\text{N}_2\text{O}_4(g)$ has dissociated to $\text{NO}_2(g)$.

- Calculate the value of K_p for this dissociation reaction at 25°C .
- If the volume of the cylinder is increased until the total pressure is 1.0 atm (the temperature of the system remains constant), calculate the equilibrium pressure of $\text{N}_2\text{O}_4(g)$ and $\text{NO}_2(g)$.
- What percentage (by moles) of the original $\text{N}_2\text{O}_4(g)$ is dissociated at the new equilibrium position (total pressure = 1.00 atm)?

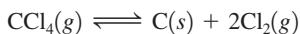
620 Chapter Thirteen Chemical Equilibrium

- 89.** A sample of gaseous nitrosyl bromide, NOBr, was placed in a rigid flask, where it decomposed at 25°C according to the following reaction:



At equilibrium the total pressure and the density of the gaseous mixture were found to be 0.0515 atm and 0.1861 g/L, respectively. Calculate the value of K_p for this reaction.

- 90.** The equilibrium constant K_p for the reaction

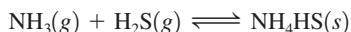


at 700°C is 0.76 atm. Determine the initial pressure of carbon tetrachloride that will produce a total equilibrium pressure of 1.20 atm at 700°C.

Integrative Problems

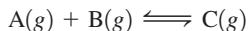
These problems require the integration of multiple concepts to find the solutions.

- 91.** For the reaction

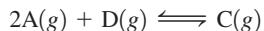


$K = 400$, at 35.0°C. If 2.00 mol each of NH₃, H₂S, and NH₄HS are placed in a 5.00-L vessel, what mass of NH₄HS will be present at equilibrium? What is the pressure of H₂S at equilibrium?

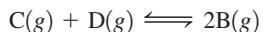
- 92.** Given $K = 3.50$ at 45°C for the reaction



and $K = 7.10$ at 45°C for the reaction



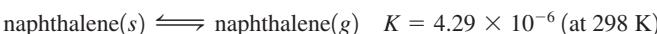
what is the value of K at the same temperature for the reaction



What is the value of K_p at 45°C for the reaction? Starting with 1.50 atm partial pressures of both C and D, what is the mole fraction of B once equilibrium is reached?

- 93.** The hydrocarbon naphthalene was frequently used in mothballs until recently, when it was discovered that human inhalation of naphthalene vapors can lead to hemolytic anemia. Naphthalene is 93.71% carbon by mass and a 0.256-mol sample of naphthalene has a mass of 32.8 g. What is the molecular formula of naphthalene? This compound works as a pesticide in mothballs by

sublimation of the solid so that it fumigates enclosed spaces with its vapors according to the equation

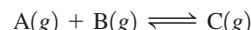


If 3.00 g of solid naphthalene is placed into an enclosed space with a volume of 5.00 L at 25°C, what percentage of the naphthalene will have sublimed once equilibrium has been established?

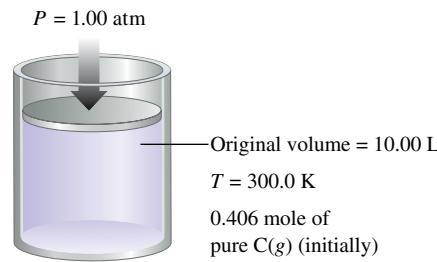
Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

- 94.** Consider the reaction



for which $K = 1.30 \times 10^2$. Assume that 0.406 mol C(g) is placed in the cylinder represented below. The temperature is 300.0 K, and the barometric pressure on the piston (which is assumed to be massless and frictionless) is constant at 1.00 atm. The original volume (before the 0.406 mol C(g) begins to decompose) is 10.00 L. What is the volume in the cylinder at equilibrium?



Get help understanding core concepts and visualizing molecular-level interactions, and practice problem solving, by visiting the Online Study Center at college.hmco.com/PIC/zumdahl7e.

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14 Acids and Bases

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A Summary



This grass pink orchid thrives in the acidic soil of a bog meadow at Illinois Beach State Park.

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 exists 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 in industry. 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.

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 (see the Chemical Impact in Chapter 5). This problem is complex and has diplomatic and economic overtones that make it all the more difficult to solve.

14.1 The Nature of Acids and Bases

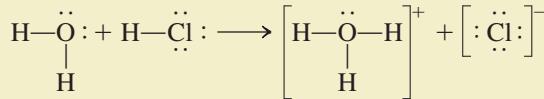
Don't taste chemicals!

Acids and bases were first discussed in Section 4.2.

Acids were first recognized as a class of 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 taste and slippery feel. Commercial preparations for unclogging drains are highly basic.

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 Brønsted (1879–1947) and the English chemist Thomas Lowry (1874–1936). In terms of the **Brønsted–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 Brønsted–Lowry acid. The molecule that accepts the proton, in this case water, is a Brønsted–Lowry base.

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:



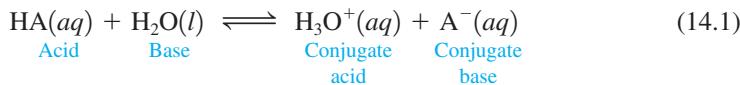
Note that the proton is transferred from the HCl molecule to the water molecule to form H_3O^+ , which is called the **hydronium ion**. This reaction is represented in Fig. 14.1 using molecular models.



Common household substances that contain acids and bases. Vinegar is a dilute solution of acetic acid. Drain cleaners contain strong bases such as sodium hydroxide.

Recall that (aq) means the substance is hydrated.

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



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 H₂O and H₃O⁺. This reaction is represented by molecular models in Fig. 14.2.

It is important to note that Equation (14.1) really represents *a competition for the proton between the two bases H₂O and A⁻*. If H₂O is a much stronger base than A⁻, that is, if H₂O 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 H₂O, 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

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$
(14.2)

where K_a is called the **acid dissociation constant**. Both H₃O^{+(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



FIGURE 14.1

The reaction of HCl and H₂O.

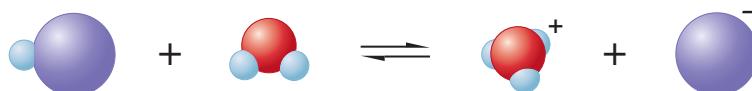


Visualization: Acid Ionization Equilibrium

In this chapter we will always represent an acid as simply dissociating. This does not mean we are using the Arrhenius model for acids. Since water does not affect the equilibrium position, it is simply easier to leave it out of the acid dissociation reaction.

FIGURE 14.2

The reaction of an acid HA with water to form H_3O^+ and a conjugate base A^- .



concentration of liquid water remains essentially constant when an acid is dissolved. Thus the term $[\text{H}_2\text{O}]$ is not included in Equation (14.2), and the equilibrium expression for K_a has the same form as that for the simple dissociation into ions:



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

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

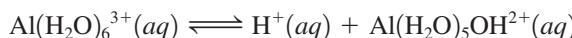
Acid Dissociation (Ionization) Reactions

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

- Hydrochloric acid (HCl)
- Acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$)
- The ammonium ion (NH_4^+)
- The anilinium ion ($\text{C}_6\text{H}_5\text{NH}_3^+$)
- The hydrated aluminum(III) ion $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$

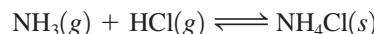
Solution

- $\text{HCl}(aq) \rightleftharpoons \text{H}^+(aq) + \text{Cl}^-(aq)$
- $\text{HC}_2\text{H}_3\text{O}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$
- $\text{NH}_4^+(aq) \rightleftharpoons \text{H}^+(aq) + \text{NH}_3(aq)$
- $\text{C}_6\text{H}_5\text{NH}_3^+(aq) \rightleftharpoons \text{H}^+(aq) + \text{C}_6\text{H}_5\text{NH}_2(aq)$
- Although this formula looks complicated, writing the reaction is simple if you concentrate on the meaning of K_a . Removing a proton, which can come only from one of the water molecules, leaves one OH^- and five H_2O molecules attached to the Al^{3+} ion. So the reaction is

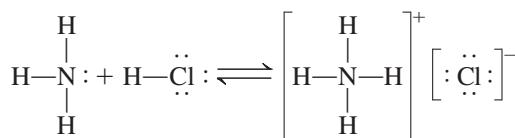


See Exercises 14.27 and 14.28.

The Brønsted-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):



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



When $\text{HCl}(g)$ and $\text{NH}_3(g)$ meet in a tube, a white ring of $\text{NH}_4\text{Cl}(s)$ forms.

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FIGURE 14.3

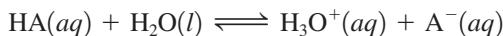
The reaction of NH_3 with HCl to form NH_4^+ and Cl^- .



Note that this is not considered an acid–base reaction according to the Arrhenius concept. Figure 14.3 shows a molecular representation of this reaction.

14.2 Acid Strength

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



A strong acid has a weak conjugate base.

A **strong acid** is one for which *this equilibrium lies far to the right*. This means that almost all the original HA is dissociated (ionized) at equilibrium [see Fig. 14.4(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 also can be described as an acid whose conjugate base is a much weaker base than water (see Fig. 14.5). In this case the water molecules win the competition for the H⁺ ions.

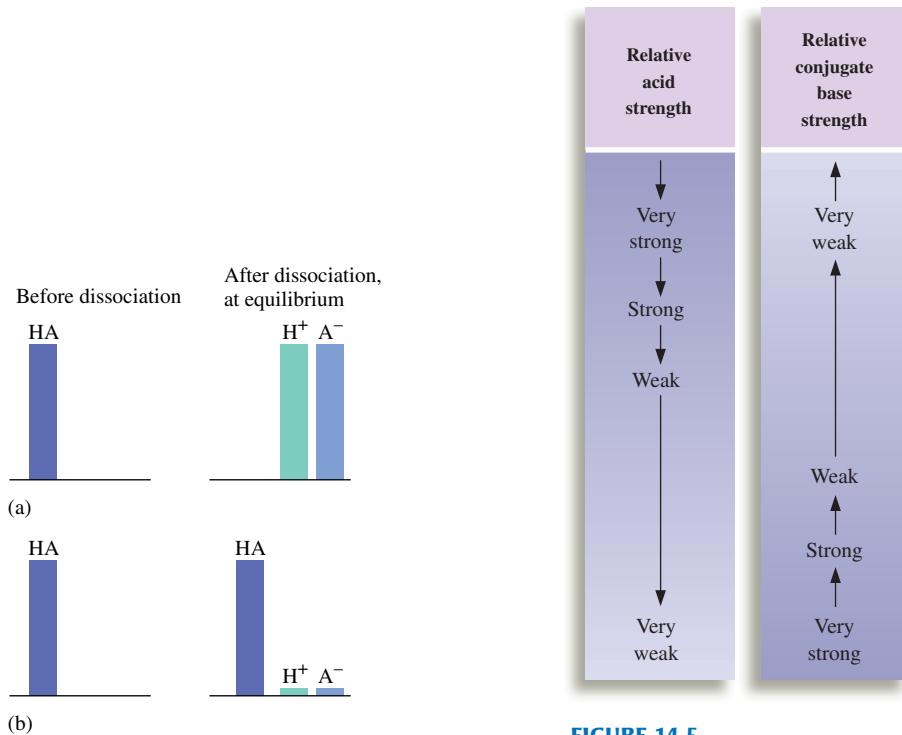


FIGURE 14.4
Graphic representation of the behavior of acids of different strengths in aqueous solution. (a) A strong acid. (b) A weak acid.

FIGURE 14.5
The relationship of acid strength and conjugate base strength for the reaction

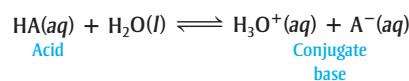


TABLE 14.1 Various Ways to Describe Acid Strength

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

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

Perchloric acid can explode if handled improperly.

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. 14.4(b)]. In contrast to a strong acid, a weak acid has a conjugate base 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. *The weaker the acid, the stronger its conjugate base.*

The various ways of describing the strength of an acid are summarized in Table 14.1. Strong and weak acids are represented pictorially in Fig. 14.6.

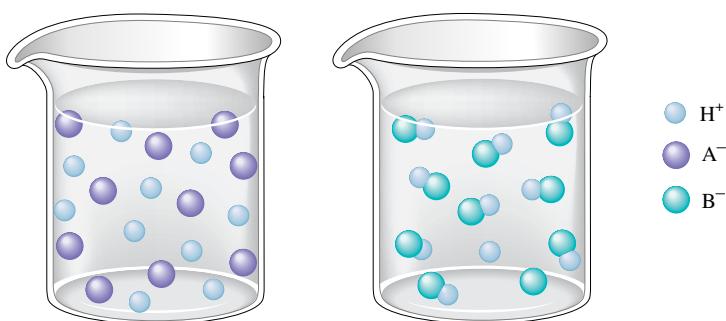
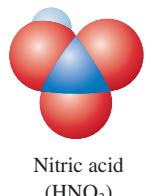
The common strong acids are sulfuric acid [$H_2SO_4(aq)$], hydrochloric acid [$HCl(aq)$], nitric acid [$HNO_3(aq)$], and perchloric acid [$HClO_4(aq)$]. Sulfuric acid is actually a **diprotic acid**, an acid having two acidic protons. The acid H_2SO_4 is a strong acid, virtually 100% dissociated (ionized)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



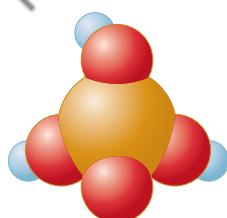
The HSO_4^- ion, however, is a weak acid:



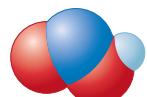
Most acids are **oxyacids**, in which the acidic proton is attached to an oxygen atom. The strong acids mentioned above, except hydrochloric acid, are typical examples. Many common weak acids, such as phosphoric acid (H_3PO_4), nitrous acid (HNO_2), and

**FIGURE 14.6**

(a) A strong acid HA is completely ionized in water. (b) A weak acid HB exists mostly as undissociated HB molecules in water. Note that the water molecules are not shown in this figure.



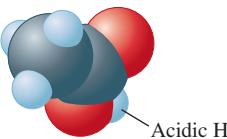
Phosphoric acid
(H_3PO_4)



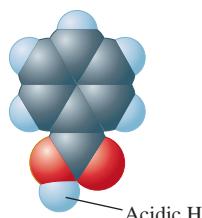
Nitrous acid
(HNO_2)



Hypochlorous acid
(HOCl)



Acetic acid
($\text{CH}_3\text{CO}_2\text{H}$)



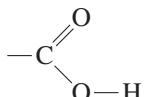
Benzoic acid
($\text{C}_6\text{H}_5\text{CO}_2\text{H}$)

TABLE 14.2 Values of K_a for Some Common Monoprotic Acids

Formula	Name	Value of K_a^*	↑ Increasing acid strength
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}	
HClO_2	Chlorous acid	1.2×10^{-2}	
$\text{HC}_2\text{H}_2\text{ClO}_2$	Monochloracetic acid	1.35×10^{-3}	
HF	Hydrofluoric acid	7.2×10^{-4}	
HNO_2	Nitrous acid	4.0×10^{-4}	
$\text{HC}_2\text{H}_3\text{O}_2$	Acetic acid	1.8×10^{-5}	
$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$	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}	

*The units of K_a are customarily omitted.

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 $\text{HC}_2\text{H}_3\text{O}_2$, and benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$). Note that the remainder of the hydrogens in these molecules are not acidic—they do not form H^+ in water.

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



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

$$K_a = \frac{[\text{H}^+][\text{Cl}^-]}{[\text{HCl}]}$$

Very small and
highly uncertain

Appendix 5.1 contains a table of K_a values.

Sample Exercise 14.2

Relative Base Strength

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

Solution

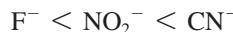
Remember that water is a stronger base than the conjugate base of a strong acid but a weaker base than the conjugate base of a weak acid. This leads to the following order:



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



the base strengths increase as follows:



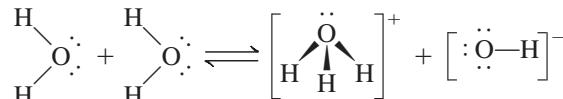
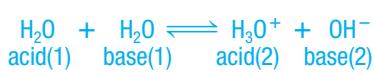
The combined order of increasing base strength is



See Exercises 14.33 through 14.36.

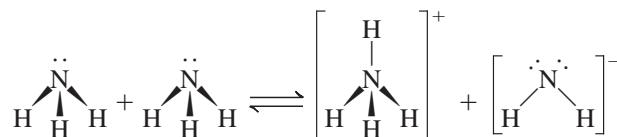
Water as an Acid and a Base

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, also illustrated in Fig. 14.7, 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



leads to the equilibrium expression

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}^+][\text{OH}^-]$$

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

Experiment shows that at 25°C in pure water,

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

which means that at 25°C

$$\begin{aligned} K_w &= [\text{H}^+][\text{OH}^-] \\ &= 1.0 \times 10^{-14} \end{aligned}$$

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

FIGURE 14.7

Two water molecules react to form H_3O^+ and OH^- .



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

Calculating $[H^+]$ and $[OH^-]$

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. $1.0 \times 10^{-5} M OH^-$
- b. $1.0 \times 10^{-7} M OH^-$
- c. $10.0 M H^+$

Solution

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

See Exercises 14.37 and 14.38.

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

Autoionization of Water

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

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



is exothermic or endothermic.

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



Visualization: Self-Ionization of Water

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 ,

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

For a neutral solution,

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

See Exercise 14.39.

**Visualization: The pH Scale**

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

Appendix 1.2 has a review of logs.

14.3 The pH Scale

Because $[\text{H}^+]$ 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

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

Thus for a solution where

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

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

$$\begin{aligned} [\text{H}^+] &= 1.0 \times 10^{-9} M \\ \text{pH} &= 9.00 \\ &\quad \text{2 significant figures} \\ &\quad \text{2 decimal places} \end{aligned}$$

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

$$\begin{aligned} \text{pOH} &= -\log[\text{OH}^-] \\ \text{pK} &= -\log K \end{aligned}$$

Since pH is a log scale based on 10, *the pH changes by 1 for every power of 10 change in $[\text{H}^+]$* . 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 $-\log[\text{H}^+]$, *the pH decreases as $[\text{H}^+]$ increases*. The pH scale and the pH values for several common substances are shown in Fig. 14.8.

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 electric potential results, which is registered on the meter (see Fig. 14.9).

Sample Exercise 14.5

Calculating pH and pOH

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

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

The pH meter is discussed more fully in Section 17.4.



CHEMICAL IMPACT

Arnold Beckman, Man of Science

Arnold Beckman died at age 104 in May 2004. Beckman's leadership of science and business spans virtually the entire twentieth century. He was born in 1900 in Cullom, Illinois, a town of 500 people that had no electricity or telephones. Beckman says, "In Cullom we were forced to improvise. I think it was a good thing."

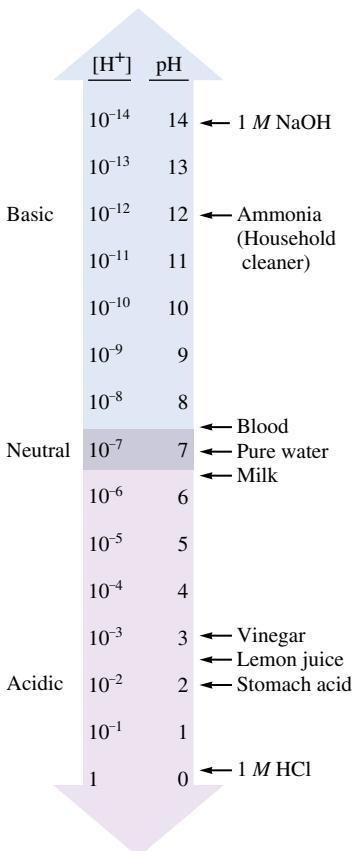
The son of a blacksmith, Beckman had his interest in science awakened at age nine. At that time, in the attic of his house he discovered *J. Dorman Steele's Fourteen Weeks in Chemistry*, a book containing instructions for doing chemistry experiments. Beckman became so fascinated with chemistry that his father built him a small "chemistry shed" in the back yard for his tenth birthday.

Beckman's interest in chemistry was fostered by his high school teachers, and he eventually attended the University of Illinois, Urbana-Champaign. He graduated with



Arnold Beckman.

a bachelor's degree in chemical engineering in 1922 and stayed one more year to get a master's degree. He then went to Caltech, where he earned a Ph.D. and became a faculty member.



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.

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

$$pH = -\log[H^+] = -\log(1.0) = 0.00$$

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

See Exercise 14.41.

It is useful to consider the log form of the expression

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



FIGURE 14.8

The pH scale and pH values of some common substances.

FIGURE 14.9

pH meters are used to measure acidity.

Beckman was always known for his inventiveness. As a youth he designed a pressurized fuel system for his Model T Ford to overcome problems with its normal gravity feed fuel system—you had to *back* it up steep hills to keep it from starving for fuel. In 1927 he applied for his first patent: a buzzer to alert drivers that they were speeding.

In 1935 Beckman invented something that would cause a revolution in scientific instrumentation. A college friend who worked in a laboratory in the California citrus industry needed an accurate, convenient way to measure the acidity of orange juice. In response, Beckman invented the pH meter, which he initially called the acidimeter. This compact, sturdy device was an immediate hit. It signaled a new era in scientific instrumentation. In fact, business was so good that Beckman left Caltech to head his own company.

Over the years Beckman invented many other devices, including an improved potentiometer and an instrument for measuring the light absorbed by molecules. At age 65 he retired as president of Beckman Instruments (headquartered in Fullerton, California). After a merger the company be-

came Beckman Coulter; it had sales of more than \$2 billion in 2003.

After stepping down as president of Beckman Instruments, Beckman began a new career—donating his wealth for the improvement of science. In 1984 he and Mabel, his wife of 58 years, donated \$40 million to his alma mater—the University of Illinois—to fund the Beckman Institute. The Beckmans have also funded many other research institutes, including one at Caltech, and formed a foundation that currently gives \$20 million each year to various scientific endeavors.

Arnold Beckman was a man known for his incredible creativity but even more he was recognized as a man of absolute integrity. Mr. Beckman has important words for us: “Whatever you do, be enthusiastic about it.”

Note: You can see Arnold Beckman’s biography at the Chemical Heritage Foundation Web site (<http://www.chemheritage.org>).

That is,

$$\begin{aligned} \log K_w &= \log[H^+] + \log[OH^-] \\ \text{or} \quad -\log K_w &= -\log[H^+] - \log[OH^-] \\ \text{Thus} \quad pK_w &= pH + pOH \end{aligned} \tag{14.3}$$

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:

$$pH + pOH = 14.00 \tag{14.4}$$

Sample Exercise 14.6

Calculating pH

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 $pH + pOH = 14.00$,

$$pOH = 14.00 - pH = 14.00 - 7.41 = 6.59$$

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

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

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,

$$\text{antilog}(n) = \log^{-1}(n)$$

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

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

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

and $[\text{H}^+]$ can be calculated by taking the antilog of $-\text{pH}$:

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

In the present case,

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

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

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

See Exercises 14.42 through 14.46.

Now that we have considered all 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 sometimes 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

When we deal with acid–base equilibria, *we must 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

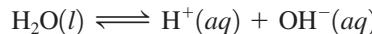
Common Strong Acids
 HCl(aq)
 $\text{HNO}_3(\text{aq})$
 $\text{H}_2\text{SO}_4(\text{aq})$
 $\text{HClO}_4(\text{aq})$

Always write the major species present in the solution.

The H⁺ from the strong acid drives the equilibrium $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ to the left.

only in tiny amounts and is classified 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.*

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 H₂O. 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, H₂O also furnishes H⁺ by autoionization, which is often represented by the simple dissociation reaction



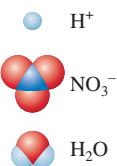
However, is autoionization an important source of H⁺ ions? In pure water at 25°C, [H⁺] is 10⁻⁷ M. In 1.0 M HCl solution, the water will produce even less than 10⁻²⁷ M H⁺, since by Le Châtelier's principle the H⁺ from the dissociated HCl will drive the position of the water equilibrium to the left. Thus the amount of H⁺ contributed by water is negligible compared with the 1.0 M H⁺ from the dissociation of HCl. Therefore, we can say that [H⁺] in the solution is 1.0 M. The pH is then

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

Sample Exercise 14.7

In pure water, only 10⁻⁷ M H⁺ is produced.

Major Species



pH of Strong Acids

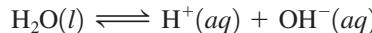
- Calculate the pH of 0.10 M HNO₃.
- Calculate the pH of 1.0 × 10⁻¹⁰ M HCl.

Solution

- Since HNO₃ is a strong acid, the major species in solution are



The concentration of HNO₃ 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



to the left. That is, this is an acidic solution where [H⁺] ≫ [OH⁻], so [OH⁻] ≪ 10⁻⁷ M. The sources of H⁺ are

- H⁺ from HNO₃ (0.10 M)
- H⁺ from H₂O

The number of H⁺ ions contributed by the autoionization of water will be very small compared with the 0.10 M contributed by the HNO₃ and can be neglected. Since the dissolved HNO₃ is the only important source of H⁺ ions in this solution,

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

- Normally, in an aqueous solution of HCl the major species are H⁺, Cl⁻, and H₂O. However, in this case the amount of HCl in solution is so small that it has no effect; the only major species is H₂O. Thus the pH will be that of pure water, or pH = 7.00.

See Exercises 14.47 and 14.48.

14.5 Calculating the pH of Weak Acid Solutions

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 unnecessary, they will become

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

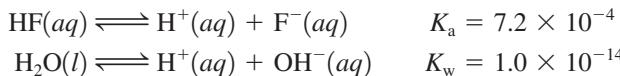
Major Species



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 ($K_a = 7.2 \times 10^{-4}$).

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 H₂O.

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:



In aqueous solutions, however, typically one source of H⁺ can be singled out as dominant. By comparing K_a for HF with K_w for H₂O, 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:



The equilibrium expression is

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

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

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

(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 this 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 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 :

$$[\text{HF}] = [\text{HF}]_0 - x = 1.00 - x$$

$$[\text{F}^-] = [\text{F}^-]_0 + x = 0 + x = x$$

$$[\text{H}^+] = [\text{H}^+]_0 + x \approx 0 + x = x$$

Substituting these equilibrium concentrations into the equilibrium expression gives

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

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

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

The validity of an approximation should always be checked.

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 $\pm 5\%$. It is reasonable therefore to apply this figure when determining the validity of the approximation

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

We will use the following test. First, we calculate the value of x by making the approximation

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

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

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 small enough that the approximation

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

will be considered valid.

In our example,

$$x = 2.7 \times 10^{-2} \text{ mol/L}$$

$$[HA]_0 = [HF]_0 = 1.00 \text{ mol/L}$$

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

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

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

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

- **1** List the major species in the solution.
- **2** Choose the species that can produce H^+ , and write balanced equations for the reactions producing H^+ .
- **3** Using the values of the equilibrium constants for the reactions you have written, decide which equilibrium will dominate in producing H^+ .
- **4** Write the equilibrium expression for the dominant equilibrium.

The K_a values for various weak acids are given in Table 14.2 and in Appendix 5.1.

- 5 List the initial concentrations of the species participating in the dominant equilibrium.
- 6 Define the change needed to achieve equilibrium; that is, define x .
- 7 Write the equilibrium concentrations in terms of x .
- 8 Substitute the equilibrium concentrations into the equilibrium expression.
- 9 Solve for x the “easy” way, that is, by assuming that $[HA]_0 - x \approx [HA]_0$.
- 10 Use the 5% rule to verify whether the approximation is valid.
- 11 Calculate $[H^+]$ and pH.

We use this systematic approach in Sample Exercise 14.8.

Sample Exercise 14.8

The pH of Weak Acids

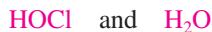
The hypochlorite ion (OCl^-) is a strong oxidizing agent often found in household bleaches and disinfectants. It is also the active ingredient that forms when swimming pool water is treated with chlorine. In addition to its oxidizing abilities, the hypochlorite ion has a relatively high affinity for 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.

Major Species

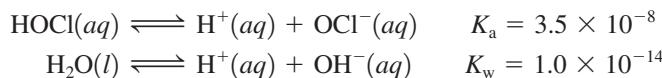


Solution

- 1 We list the major species. Since $HOCl$ is a weak acid and remains mostly undisassociated, the major species in a 0.100 M $HOCl$ solution are



- 2 Both species can produce H^+ :



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

- 4 We therefore use the following equilibrium expression:

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

- 5 The initial concentrations appropriate for this equilibrium are

$$[HOCl]_0 = 0.100\text{ M}$$

$$[OCl^-]_0 = 0$$

$$[H^+]_0 \approx 0 \quad (\text{We neglect the contribution from } H_2O.)$$

- 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.

- 7 The equilibrium concentrations in terms of x are

$$[HOCl] = [HOCl]_0 - x = 0.100 - x$$

$$[OCl^-] = [OCl^-]_0 + x = 0 + x = x$$

$$[H^+] = [H^+]_0 + x \approx 0 + x = x$$

- 8 Substituting these concentrations into the equilibrium expression gives

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



Swimming pool water must be frequently tested for pH and chlorine content.

→ 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

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

→ 10 The approximation $0.100 - x \approx 0.100$ must be validated. To do this, we compare x to $[\text{HOCl}]_0$:

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

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

→ 11 We calculate $[\text{H}^+]$ and pH:

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

See Exercises 14.53 through 14.55.

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

The pH of Weak Acid Mixtures

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.

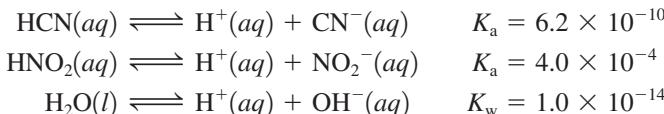
Solution

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

Major Species



All three of these components produce H^+ :



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

$$K_a = 4.0 \times 10^{-4} = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

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

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[\text{HNO}_2]_0 = 5.00$		$[\text{HNO}_2] = 5.00 - x$
$[\text{NO}_2^-]_0 = 0$	$\xrightarrow{x \text{ mol/L HNO}_2}$ dissociates	$[\text{NO}_2^-] = x$
$[\text{H}^+]_0 \approx 0$		$[\text{H}^+] = x$

It is convenient to represent these concentrations in the following shorthand form (called an ICE table):

	$\text{HNO}_2(aq)$	\rightleftharpoons	$\text{H}^-(aq)$	+	$\text{NO}_2^-(aq)$
Initial:	5.00		0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$5.00 - x$		x		x

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

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

We solve for x :

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

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

$$\frac{x}{[\text{HNO}_2]_0} \times 100 = \frac{4.5 \times 10^{-2}}{5.00} \times 100 = 0.90\%$$

Therefore,

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

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:



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

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

We know $[\text{H}^+]$ for this solution from the results of 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 $[\text{H}^+]$ we need to insert into the HCN equilibrium expression is $4.5 \times 10^{-2} M$, even though the H^+ was contributed almost entirely from the dissociation of HNO_2 . What is $[\text{HCN}]$ at equilibrium? We know $[\text{HCN}]_0 = 1.00 M$, and since K_a for HCN is so small, a negligible amount of HCN will dissociate. Thus

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

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 dissociated. This is a very small amount compared with 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.

See Exercises 14.61 and 14.62.

Percent Dissociation

Percent dissociation is also known as *percent ionization*.

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:

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

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 demonstrated in Sample Exercise 14.10.

Sample Exercise 14.10

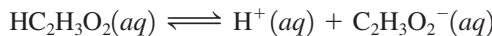
Calculating Percent Dissociation

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

- $1.00 M HC_2H_3O_2$
- $0.100 M HC_2H_3O_2$

Solution

- 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 a much stronger acid than water. Thus the dominant equilibrium will be



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 equilibrium concentrations are:

	$HC_2H_3O_2(aq)$	\rightleftharpoons	$H^+(aq)$	+	$C_2H_3O_2^-(aq)$
Initial:	1.00		0		0
Change:	$-x$		x		x
Equilibrium:	$1.00 - x$		x		x



An acetic acid solution, which is a weak electrolyte, contains only a few ions and does not conduct as much current as a strong electrolyte. The bulb is only dimly lit.

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

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

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

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 (check this yourself), 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 $[HC_2H_3O_2] = 0.100 M$. 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

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

See Exercises 14.63 and 14.64.

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.

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

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

$$[H^+] = [A^-] = x$$

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

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

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

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

and Q , the reaction quotient, is

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

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



CHEMICAL IMPACT

Household Chemistry

Common household bleach is an aqueous solution containing approximately 5% sodium hypochlorite, a potent oxidizing agent that can react with and decolorize chemicals that cause stains. Bleaching solutions are manufactured by dissolving chlorine gas in a sodium hydroxide solution to give the reaction



As long as the pH of this solution is maintained above 8, the OCl^- ion is the predominant chlorine-containing species. However, if the solution is made acidic (the $[\text{OH}^-]$ lowered), elemental chlorine (Cl_2) is favored, and since Cl_2 is much less soluble in water than is sodium hypochlorite, Cl_2 gas is suddenly evolved from the solution. This is why labels on bottles of bleach carry warnings about mixing the bleach with other cleaning solutions. For example, toilet bowl cleaners usually contain acids such as H_3PO_4 or HSO_4^- and have pH values around 2. Mixing toilet bowl cleaner with bleach can lead to a very dangerous evolution of chlorine gas.

In addition, if bleach is mixed with a cleaning agent containing ammonia, the chlorine and ammonia can react to produce chloramines, such as NH_2Cl , NHCl_2 , and NCl_3 . These compounds produce acrid fumes that can cause respiratory distress.

HOUSEHOLD USE

Toilet bowls. Flush toilet. Pour 1 cup of bleach into bowl. Brush. Let stand 10 minutes before flushing again.

Kitchen sinks. Cover stains with 1 gallon of water before adding 2/3 cup of Safeway Regular Ultra Bleach. Let stand 5 minutes before rinsing.

Bathtubs and showers, floors, vinyl, tile, woodwork and appliances. Clean with a solution of 2/3 cup of bleach per gallon of warm water. Let stand 5 minutes before rinsing.

DANGER: CORROSIVE.

Contains Sodium Hypochlorite

Contains No Phosphates

Causes substantial but temporary eye injury. Avoid contact with eyes or on clothing. Harmful if swallowed. May irritate skin. For prolonged use, wear gloves. Treatment: If in eyes rinse with plenty of water for 15 minutes. If swallowed, drink a glassful of water. Call physician or Poison Control Center in either case. If in contact with skin wash skin thoroughly with soap and water.

Add only to water, do not mix with acid or other household chemicals such as toilet bowl cleaners, ammonia or rust removers. To do so may release hazardous gases. Prolonged contact with metal may cause pitting or discoloration.

Storage and disposal: Store in a cool dry area, away from direct sunlight and heat to avoid deterioration. Do not reuse empty container; instead, rinse and put in trash collection.

The label on this bleach bottle warns of the hazards of mixing cleaning solutions.

is summarized in Fig. 14.10. In Sample Exercise 14.11 we see how the percent dissociation can be used to calculate the K_a value for a weak acid.

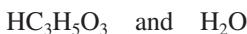
Sample Exercise 14.11

Calculating K_a from Percent Dissociation

Lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$) 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 $\text{HC}_3\text{H}_5\text{O}_3$ is a weak acid. Thus the major species in the solution are the undissociated acid and water:



However, even though $\text{HC}_3\text{H}_5\text{O}_3$ is a weak acid, it is a much stronger acid than water and will be the dominant source of H^+ in the solution. The dissociation reaction is



and the equilibrium expression is

$$K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]}$$

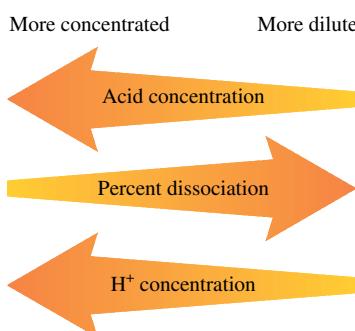


FIGURE 14.10

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

Major Species



Strenuous exercise causes a buildup of lactic acid in muscle tissues.

In a basic solution at 25°C, $\text{pH} > 7$.



Visualization: Limewater and Carbon Dioxide

The initial and equilibrium concentrations are as follows:

Initial Concentration (mol/L)	Equilibrium Concentration (mol/L)
$[\text{HC}_3\text{H}_5\text{O}_3]_0 = 0.10$	$[\text{HC}_3\text{H}_5\text{O}_3] = 0.10 - x$
$[\text{C}_3\text{H}_5\text{O}_3^-]_0 = 0$	$[\text{C}_3\text{H}_5\text{O}_3^-] = x$
$[\text{H}^+]_0 \approx 0$	$[\text{H}^+] = x$

$\xrightarrow{\text{x mol/L}}$
 $\text{HC}_3\text{H}_5\text{O}_3$
dissociates

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

$$\text{Percent dissociation} = 3.7\% = \frac{x}{[\text{HC}_3\text{H}_5\text{O}_3]_0} \times 100\% = \frac{x}{0.10} \times 100\%$$

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

Now we can calculate the equilibrium concentrations:

$$[\text{HC}_3\text{H}_5\text{O}_3] = 0.10 - x = 0.10 \text{ M} \quad (\text{to the correct number of significant figures})$$

$$[\text{C}_3\text{H}_5\text{O}_3^-] = [\text{H}^+] = x = 3.7 \times 10^{-3} \text{ M}$$

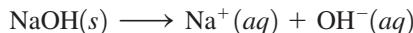
These concentrations can now be used to calculate the value of K_a for lactic acid:

$$K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{(3.7 \times 10^{-3})(3.7 \times 10^{-3})}{0.10} = 1.4 \times 10^{-4}$$

See Exercises 14.65 and 14.66.

14.6 Bases

According to the Arrhenius concept, a base is a substance that produces OH^- ions in aqueous solution. According to the Brønsted-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 strong electrolytes, dissociate completely when dissolved in aqueous solution:



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— $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, and $\text{Sr}(\text{OH})_2$ —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

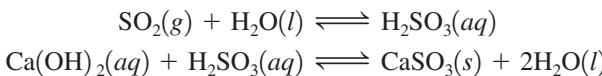


An antacid containing aluminum and magnesium hydroxides.

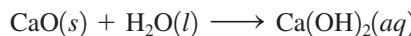
Calcium carbonate is also used in scrubbing, as discussed in Section 5.10.

hydroxide ion to react with the stomach acid, since the salts dissolve as this reaction proceeds.

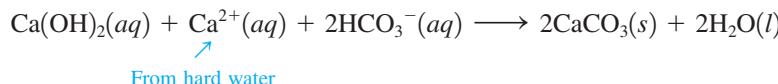
Calcium hydroxide, $\text{Ca}(\text{OH})_2$, often called **slaked lime**, is widely used in industry because it is inexpensive and plentiful. For example, slaked lime is used in scrubbing stack gases to remove sulfur dioxide from the exhaust of power plants and factories. In the scrubbing process a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



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+} , that 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, that is,



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



Thus, for every mole of $\text{Ca}(\text{OH})_2$ 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

The pH of Strong Bases

Calculate the pH of a $5.0 \times 10^{-2} M$ NaOH solution.

Solution

The major species in this solution are



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,

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

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

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

$$\text{pH} = 12.70$$

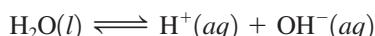
Note that this is a basic solution for which

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

Major Species



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

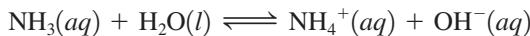


to the left, significantly lowering $[\text{H}^+]$ compared with that in pure water.

See Exercises 14.77 through 14.80.

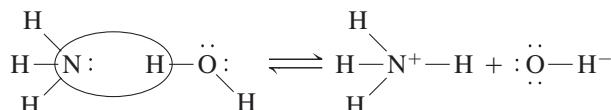
A base does not have to contain hydroxide ion.

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:

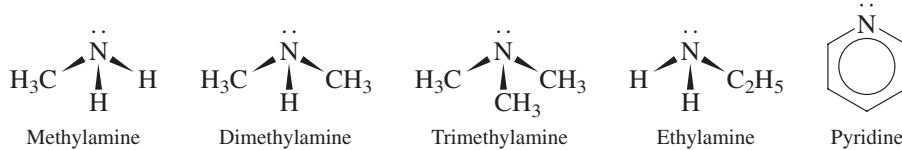


The ammonia molecule accepts a proton and thus functions as a base. Water is the acid in this reaction. Note that even though the base ammonia contains no hydroxide ion, it still increases the concentration of hydroxide ion to yield a basic solution.

Bases such as 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:



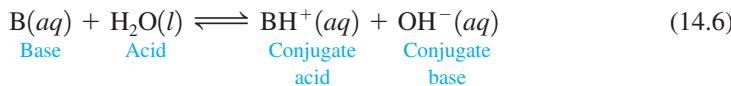
There are many bases like ammonia that produce hydroxide ion by reaction with water. In most of these bases, the lone pair is located on a nitrogen atom. Some examples are



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



The equilibrium constant for this general reaction is

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

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.

Appendix 5.3 contains a table of K_b values.

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	$\text{C}_2\text{H}_5\text{NH}_2$	$\text{C}_2\text{H}_5\text{NH}_3^+$	5.6×10^{-4}
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	$\text{C}_6\text{H}_5\text{NH}_3^+$	3.8×10^{-10}
Pyridine	$\text{C}_5\text{H}_5\text{N}$	$\text{C}_5\text{H}_5\text{NH}^+$	1.7×10^{-9}



Visualization: Brønsted–Lowry Reaction

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

The pH of Weak Bases I

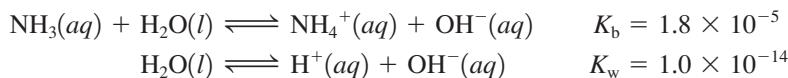
Calculate the pH for a 15.0 M solution of NH_3 ($K_b = 1.8 \times 10^{-5}$).

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



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



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

$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

The appropriate concentrations are

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

Initial Concentration (mol/L)	Equilibrium Concentration (mol/L)		
$[\text{NH}_3]_0 = 15.0$	$x \text{ mol/L}$	$[\text{NH}_3] = 15.0 - x$	
$[\text{NH}_4^+]_0 = 0$	$\xrightarrow{\text{NH}_3 \text{ reacts with H}_2\text{O to reach equilibrium}}$	$[\text{NH}_4^+] = x$	
$[\text{OH}^-]_0 \approx 0$		$[\text{OH}^-] = x$	

In terms of an ICE table, these concentrations are:

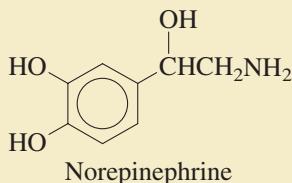
	$\text{NH}_3(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{NH}_4^+(aq)$	+	$\text{OH}^-(aq)$
Initial:	15.0		—		0		0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$15.0 - x$		—		x		x



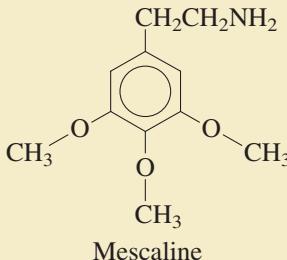
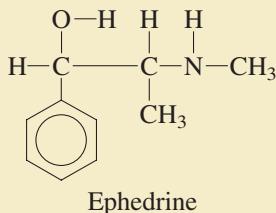
CHEMICAL IMPACT

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*.



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 the peyote cactus, for centuries.



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

$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(x)(x)}{15.0 - x} \approx \frac{x^2}{15.0}$$

Thus

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

The 5% rule validates the approximation (check it yourself), so

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

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

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

Therefore,

$$\text{pH} = -\log(6.3 \times 10^{-13}) = 12.20$$

See Exercises 14.83 and 14.84.

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

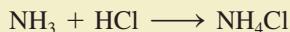
1. We calculated $[\text{H}^+]$ from K_w and then calculated the pH, but another method is available. The pOH could have been calculated from $[\text{OH}^-]$ and then used in Equation (14.3):

$$\text{p}K_w = 14.00 = \text{pH} + \text{pOH}$$

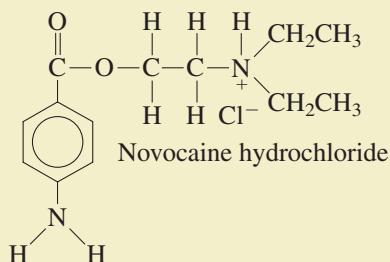
$$\text{pH} = 14.00 - \text{pOH}$$

A table of K_b values for bases is also given in Appendix 5.3.

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



Amines also can 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 anesthetic *novocaine* is insoluble in water, whereas the acid salt is much more soluble.



Peyote cactus growing on a rock.

2. In a 15.0 M NH_3 solution, the equilibrium concentrations of NH_4^+ and OH^- are each $1.6 \times 10^{-2}\text{ M}$. 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.

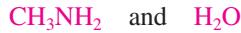
Sample Exercise 14.14

The pH of Weak Bases II

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



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



and

$$K_b = 4.38 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

Major Species



The ICE table is:

	$\text{CH}_3\text{NH}_2(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{CH}_3\text{NH}_3^+(aq)$	+	$\text{OH}^-(aq)$
Initial:	1.0		—		0		0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$1.0 - x$		—		x		x

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

$$K_b = 4.38 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{(x)(x)}{1.0 - x} \approx \frac{x^2}{1.0}$$

and

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

The approximation is valid by the 5% rule, so

$$[\text{OH}^-] = x = 2.1 \times 10^{-2} M$$

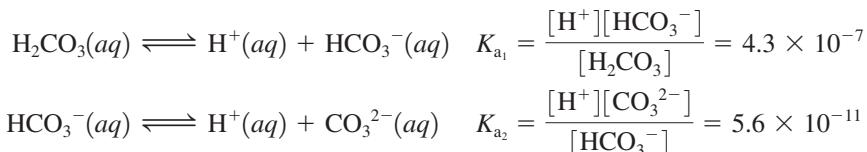
$$\text{pOH} = 1.68$$

$$\text{pH} = 14.00 - 1.68 = 12.32$$

See Exercises 14.85 and 14.86.

14.7 Polyprotic Acids

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:



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



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:

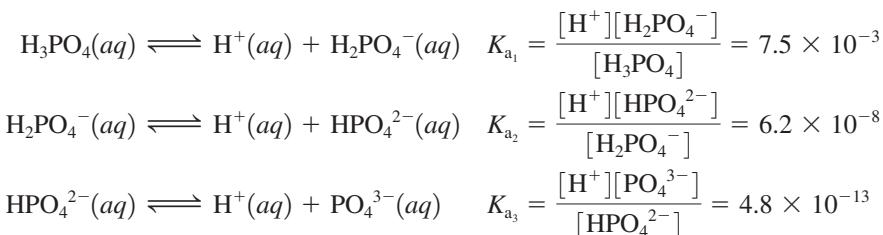


TABLE 14.4 Stepwise Dissociation Constants for Several Common Polyprotic Acids

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}	$\sim 10^{-19}$	
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	7.9×10^{-5}	1.6×10^{-12}	

*The K_{a_2} value for H_2S is very uncertain. Because it is so small, the K_{a_2} value is very difficult to measure accurately.

For a typical weak polyprotic acid,

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

A table of K_a values for polyprotic acids is also given in Appendix 5.2.

That is, the acid involved in 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 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.

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 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



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

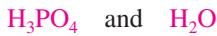
Sample Exercise 14.15

The pH of a Polyprotic Acid

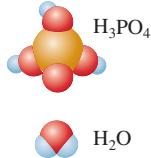
Calculate the pH of a 5.0 M H_3PO_4 solution and the equilibrium concentrations of the species H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} .

Solution

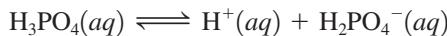
The major species in solution are



Major Species



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 is the dissociation of H_3PO_4 :



where $K_{a_1} = 7.5 \times 10^{-3} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$

The ICE table is:

	$\text{H}_3\text{PO}_4(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	+	$\text{H}_2\text{PO}_4^-(aq)$
Initial:	5.0		0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$5.0 - x$		x		x

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

$$K_{a_1} = 7.5 \times 10^{-3} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{(x)(x)}{5.0 - x} \approx \frac{x^2}{5.0}$$

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

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

$$\text{pH} = 0.72$$

So far we have determined that

$$[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.19 \text{ M}$$

and

$$[\text{H}_3\text{PO}_4] = 5.0 - x = 4.8 \text{ M}$$

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

$$K_{a_2} = 6.2 \times 10^{-8} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

where

$$[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.19 \text{ M}$$

Thus

$$[\text{HPO}_4^{2-}] = K_{a_2} = 6.2 \times 10^{-8} \text{ M}$$

To calculate $[\text{PO}_4^{3-}]$, we use the expression for K_{a_3} and the values of $[\text{H}^+]$ and $[\text{HPO}_4^{2-}]$ calculated previously:

$$K_{a_3} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 4.8 \times 10^{-13} = \frac{0.19[\text{PO}_4^{3-}]}{(6.2 \times 10^{-8})}$$

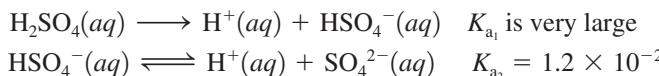
$$[\text{PO}_4^{3-}] = \frac{(4.8 \times 10^{-13})(6.2 \times 10^{-8})}{0.19} = 1.6 \times 10^{-19} \text{ M}$$

These results show that the second and third dissociation steps do not make an important contribution to $[\text{H}^+]$. This is apparent from the fact that $[\text{HPO}_4^{2-}]$ is $6.2 \times 10^{-8} \text{ M}$, which means that only $6.2 \times 10^{-8} \text{ mol/L}$ H_2PO_4^- has dissociated. The value of $[\text{PO}_4^{3-}]$ shows that the dissociation of HPO_4^{2-} is even smaller. We must, however, use the second and third dissociation steps to calculate $[\text{HPO}_4^{2-}]$ and $[\text{PO}_4^{3-}]$, since these steps are the only sources of these ions.

See Exercises 14.95 and 14.96.

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*:



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

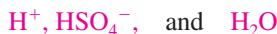
Sample Exercise 14.16

The pH of Sulfuric Acid

Calculate the pH of a 1.0 M H_2SO_4 solution.

Solution

The major species in the solution are



Major Species



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 reactions of HSO_4^- :



$$\text{where } K_{a_2} = 1.2 \times 10^{-2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

The ICE table is:

	$\text{HSO}_4^-(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	+	$\text{SO}_4^{2-}(aq)$
Initial:	1.0		1.0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$1.0 - x$		$1.0 + x$		x

Note that $[\text{H}^+]_0$ 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 give

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(1.0 + x)(x)}{1.0 - x} \approx \frac{(1.0)(x)}{(1.0)}$$

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 $[\text{H}^+]$ in this case. Instead,

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

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

$$[\text{H}^+] = 1.0 \text{ M} \quad \text{and} \quad \text{pH} = 0.00$$

See Exercise 14.97.



A bottle of sulfuric acid.

Only in dilute H₂SO₄ solutions does the second dissociation step contribute significantly to [H⁺].

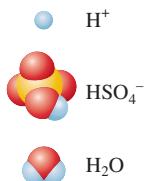
Sample Exercise 14.16 illustrates the most common case for sulfuric acid in which only the first dissociation makes an important contribution to the concentration of H⁺. In solutions more dilute than 1.0 M (for example, 0.10 M H₂SO₄), the dissociation of HSO₄⁻ is important, and solving the problem requires use of the quadratic formula, as shown in Sample Exercise 14.17.

Sample Exercise 14.17

The pH of Sulfuric Acid

Calculate the pH of a 1.00 × 10⁻² M H₂SO₄ solution.

Major Species



Solution

The major species in solution are



Proceeding as in Sample Exercise 14.16, we consider the dissociation of HSO₄⁻, which leads to the following ICE table:

	H ₂ SO ₄ ⁻ (aq)	↔	H ⁺ (aq)	+	SO ₄ ²⁻ (aq)
Initial:	0.0100		0.0100		0
		From dissociation of H ₂ SO ₄			
Change:	-x		+x		+x
Equilibrium:	0.0100 - x		0.0100 + x		x

Substituting the equilibrium concentrations into the expression for K_{a₂} 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 0.0100 + x ≈ 0.0100 and 0.0100 - x ≈ 0.0100, 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 × 10⁻², and c = -1.2 × 10⁻⁴. Use of the quadratic formula gives one negative root (which cannot be correct) and one positive root,

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

$$\text{Thus } [\text{H}^+] = 0.0100 + x = 0.0100 + 0.0045 = 0.0145 \\ \text{and } \text{pH} = 1.84$$

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

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

See Exercise 14.98.

Characteristics of Weak Polyprotic Acids

1. Typically, successive K_a values are 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 typical weak polyprotic acid is identical to that for a solution of a weak monoprotic acid.
2. 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 must be used to obtain the total H^+ concentration.

14.8 Acid–Base Properties of Salts

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 in water. 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^+ , 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 $[\text{H}^+]$ 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.

Major Species



Salts That Produce Basic Solutions

In an aqueous solution of sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$), the major species are



What are the acid–base properties of each component? The Na^+ ion has neither acid nor base properties. The $\text{C}_2\text{H}_3\text{O}_2^-$ ion is the conjugate base of acetic acid, a weak acid. This means that $\text{C}_2\text{H}_3\text{O}_2^-$ 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 $\text{C}_2\text{H}_3\text{O}_2^-$ ion. Since $\text{C}_2\text{H}_3\text{O}_2^-$ 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



Note that this reaction, which yields a base 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,

$$K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]}$$

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 :

$$K_a \times K_b = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \times \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = [\text{H}^+][\text{OH}^-] = K_w$$

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,

$$K_b = \frac{K_w}{K_a \text{ (for } \text{HC}_2\text{H}_3\text{O}_2\text{)}} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

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 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.

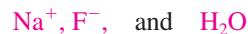
Sample Exercise 14.18

Salts as Weak Bases

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

Solution

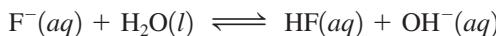
The major species in solution are



Major Species



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



which yields the K_b expression

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

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 corresponding ICE table is:

	$\text{F}^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{HF}(aq)$	+	$\text{OH}^-(aq)$
Initial:	0.30		—		0		≈ 0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$0.30 - x$		—		x		x

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

and

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

The approximation is valid by the 5% rule, so

$$[\text{OH}^-] = x = 2.0 \times 10^{-6} M$$

$$\text{pOH} = 5.69$$

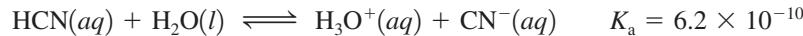
$$\text{pH} = 14.00 - 5.69 = 8.31$$

As expected, the solution is basic.

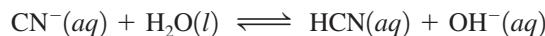
See Exercise 14.103.

Base Strength in Aqueous Solutions

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:



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:



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

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:



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:



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

In general, *salts in which the anion is not a base and the cation is the conjugate acid of a weak base produce acidic solutions.*

Sample Exercise 14.19

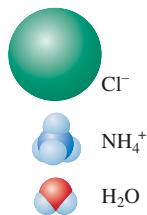
Salts as Weak Acids I

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

Major Species



Note that both NH_4^+ and H_2O can produce H^+ . The dissociation reaction for the NH_4^+ ion is



for which

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

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

$$K_a \times K_b = K_w$$

$$\text{Thus } K_a \text{ (for } \text{NH}_4^+) = \frac{K_w}{K_b \text{ (for } \text{NH}_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Although NH_4^+ is a very weak acid, as indicated by its K_a value, it is stronger than H_2O and 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:

	$\text{NH}_4^+(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	+	$\text{NH}_3(aq)$
Initial:	0.10		≈ 0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.10 - x$		x		x

Thus

$$5.6 \times 10^{-10} = K_a = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{(x)(x)}{0.10 - x} \approx \frac{x^2}{0.10}$$

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

The approximation is valid by the 5% rule, so

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

See Exercise 14.104.

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 Brønsted–Lowry acid, the hydrated ion $\text{Al}(\text{H}_2\text{O})_6^{3+}$ formed in water is a weak acid:



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

Salts as Weak Acids II

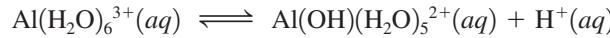
Calculate the pH of a 0.010 M AlCl_3 solution. The K_a value for $\text{Al}(\text{H}_2\text{O})_6^{3+}$ is 1.4×10^{-5} .

Solution

The major species in solution are

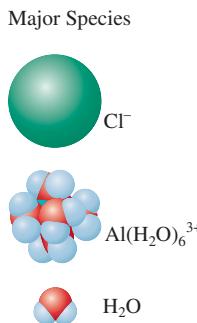


Since the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion is a stronger acid than water, the dominant equilibrium is



$$\text{and } 1.4 \times 10^{-5} = K_a = \frac{[\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}][\text{H}^+]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]}$$

This is a typical weak acid problem, which we can solve with the usual procedure:



	$\text{Al}(\text{H}_2\text{O})_6^{3+}(aq)$	\rightleftharpoons	$\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}(aq)$	+	$\text{H}^+(aq)$
I nitial:	0.010		0		≈ 0
C hange:	$-x$		$+x$		$+x$
E quilibrium:	$0.010 - x$		x		x

Thus

$$1.4 \times 10^{-5} = K_a = \frac{[\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}][\text{H}^+]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]} = \frac{(x)(x)}{0.010 - x} \approx \frac{x^2}{0.010}$$

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

Since the approximation is valid by the 5% rule,

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

See Exercises 14.109 and 14.110.

TABLE 14.5 Qualitative Prediction of pH for Solutions of Salts for Which Both Cation and Anion Have Acidic or Basic Properties

$K_a > K_b$	$\text{pH} < 7$ (acidic)
$K_b > K_a$	$\text{pH} > 7$ (basic)
$K_a = K_b$	$\text{pH} = 7$ (neutral)

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 ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$), 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 with 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.

Sample Exercise 14.21**The Acid–Base Properties of Salts**

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

- a. $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ b. NH_4CN c. $\text{Al}_2(\text{SO}_4)_3$

Solution

- a. The ions in solution are NH_4^+ and $\text{C}_2\text{H}_3\text{O}_2^-$. As we mentioned previously, K_a for NH_4^+ is 5.6×10^{-10} and K_b for $\text{C}_2\text{H}_3\text{O}_2^-$ is 5.6×10^{-10} . Thus K_a for NH_4^+ is equal to K_b for $\text{C}_2\text{H}_3\text{O}_2^-$, and the solution will be neutral ($\text{pH} = 7$).
- b. The solution will contain NH_4^+ and CN^- ions. The K_a value for NH_4^+ is 5.6×10^{-10} and

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

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 $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and SO_4^{2-} ions. The K_a value for $\text{Al}(\text{H}_2\text{O})_6^{3+}$ 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,

$$\begin{aligned} K_b(\text{for } \text{SO}_4^{2-}) &= \frac{K_w}{K_{a_2}(\text{for sulfuric acid})} \\ &= \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-2}} = 8.3 \times 10^{-13} \end{aligned}$$

This solution will be acidic, since K_a for $\text{Al}(\text{H}_2\text{O})_6^{3+}$ is much greater than K_b for SO_4^{2-} .

See Exercises 14.111 and 14.112.

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

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 acts as an acid or a base	Neutral
Cation is from strong base; anion is from weak acid	$\text{NaC}_2\text{H}_3\text{O}_2$, 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	$\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, 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	$\text{Al}(\text{NO}_3)_3$, FeCl_3	Hydrated cation acts as an acid; anion has no effect on pH	Acidic

14.9 The Effect of Structure on Acid–Base Properties

Further aspects of acid strengths are discussed in Section 20.7.

TABLE 14.7 Bond Strengths and Acid Strengths for Hydrogen Halides

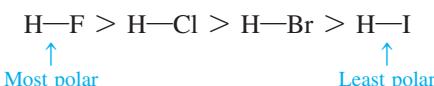
H—X Bond	Bond Strength (kJ/mol)	Acid Strength in Water
H—F	565	Weak
H—Cl	427	Strong
H—Br	363	Strong
H—I	295	Strong

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 Brønsted–Lowry acid: the strength of the bond and the polarity of the bond.

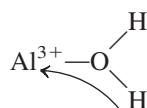
To explore these factors let's consider the relative acid strengths of the hydrogen halides. The bond polarities vary as shown



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, and thus is difficult to break. This contributes significantly to the reluctance of the HF molecules to dissociate in water.

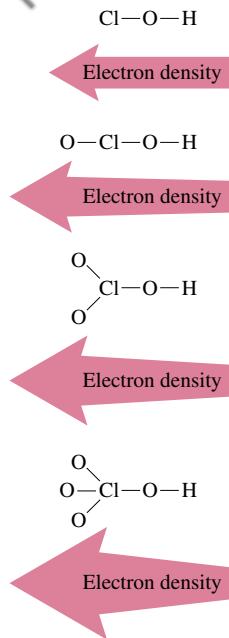
Another important class of acids are the oxyacids, which as we saw in Section 14.2 characteristically contain the grouping H—O—X. Several series of oxyacids are listed with their K_a values in Table 14.8. Note from these data that for a given series the acid strength increases with an increase in the 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. 14.11. The net effect is to both polarize and weaken the O—H bond; this effect becomes 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).

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 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.

**FIGURE 14.11**

The effect of the number of attached oxygens on the O—H 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 O—H bond, thereby weakening and polarizing it. This increases the tendency for the molecule to produce a proton, and so its acid strength increases.

TABLE 14.8 Several Series of Oxyacids and Their K_a Values

Oxyacid	Structure	K_a Value
HClO ₄	H—O—Cl—O—O	Large ($\sim 10^7$)
HClO ₃	H—O—Cl—O—O	~ 1
HClO ₂	H—O—Cl—O	1.2×10^{-2}
HClO	H—O—Cl	3.5×10^{-8}
H ₂ SO ₄	H—O—S—O—H	Large
H ₂ SO ₃	H—O—S—O—H	1.5×10^{-2}
HNO ₃	H—O—N—O	Large
HNO ₂	H—O—N—O	4.0×10^{-4}

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)	$\sim 10^{-15}$

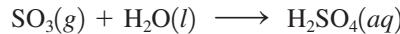
14.10 Acid–Base Properties of Oxides

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.

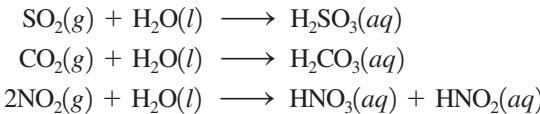
We have just seen that molecules containing the grouping H—O—X can behave as acids and that the acid strength depends on the electron-withdrawing ability of X. But substances with this grouping also can behave as bases if the hydroxide ion instead of a proton is produced. What determines which behavior 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.

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:

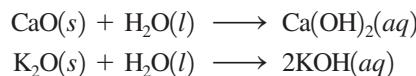


The structure of H_2SO_4 is shown in the margin. In this case, the strong, covalent O—S bonds remain intact and the H—O bonds break to produce protons. Other common covalent oxides that react with water to form acidic solutions are sulfur dioxide, carbon dioxide, and nitrogen dioxide, as shown by the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

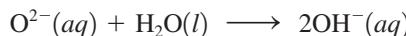


Thus, when a covalent oxide dissolves in water, an acidic solution forms. These oxides are called **acidic oxides**.

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



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:



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

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 Brønsted–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*. Another way of saying this is that a Lewis acid has an empty atomic orbital that it can use to accept (share) an electron pair from a molecule that has a lone pair of electrons (Lewis base). The three models for acids and bases are summarized in Table 14.10.

TABLE 14.10 Three Models for Acids and Bases

Model	Definition of Acid	Definition of Base
Arrhenius	H^+ producer	OH^- producer
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	Electron-pair acceptor	Electron-pair donor