

Cutting Drug Costs with Generics



Most individuals in their youthful years think very little (if at all) about the cost of medications. If a young person searches the couch cushions for change, it is generally for gas money or a soft drink. However, as we age we might find ourselves searching under couch cushions once again, this time in hopes of finding folding money to help pay for one of our numerous prescriptions.

Why are prescriptions so costly, and is there any way to get them at a lower cost? The development of new drugs usually requires years of research and substantial funding. As a result, any newly-developed drugs are under patent protection for approximately 20 years in the U.S., and their production and sale are limited to those who own the patent. Once the patent expires, others have the right to produce and market the drug in what is called a generic version. Regulations set by the Food and Drug Administration (FDA) assure that generic drugs must contain the same active ingredients as the original patented drug. However, the generic versions can be different in other ways such as the color, shape and fillers. Generic versions are generally less expensive than the original, with savings to consumers of 30 to 90 percent of the purchase price of the original drug. The amount of savings often depends on the number of generic brands on the market. To benefit from the savings, ask your doctor or pharmacist if

the medications you require are available in a less expensive generic form.



Generic drugs are sometimes different colors than the patented version.

Avogadro's law Equal volumes of gases measured at the same temperature and pressure contain equal numbers of molecules.

standard conditions (STP) A set of specific temperature and pressure values used for gas measurements.

ideal gas law A gas law that relates the pressure, volume, temperature, and number of moles in a gas sample. Mathematically, it is $PV = nRT$.



Figure 6.7 The box has a 22.4-L volume, the volume of 1 mol of any gas at STP. The basketball has a volume of 7.4 L. How many moles of gas would it contain at STP?

6.8 The Ideal Gas Law

Learning Objective

- Do calculations based on the ideal gas law.

The combined gas law (Equation 6.8) works for samples only in which the mass of gas remains constant during changes in temperature, pressure, and volume. However, it is often useful to work with situations in which the amount of gas varies. The foundation for this kind of work was proposed in 1811 by Amadeo Avogadro, an Italian scientist. According to his proposal, which is now known as **Avogadro's law**, equal volumes of different gases measured at the same temperature and pressure contain equal numbers of gas molecules. According to this idea, two identical compressed gas cylinders of helium and oxygen at the same pressure and temperature would contain identical numbers of molecules of the respective gases. However, the mass of gas in the cylinders would *not* be the same because the molecules of the two gases have different molecular weights.

The actual temperature and pressure used do not influence the validity of Avogadro's law, but it is convenient to specify a standard set of values. Chemists have chosen 0°C (273 K) and 1.00 atm to represent what are called **standard conditions** for gas measurements. These conditions are often abbreviated STP (standard temperature and pressure).

As we have seen, the mole (defined in Section 2.6) is a convenient quantity of matter to work with. What volume does 1 mol of a gas occupy according to Avogadro's law? Experiments show that 1 mol of any gas molecules has a volume of 22.4 L at STP (see Figure 6.7).

A combination of Boyle's, Charles's, and Avogadro's laws leads to another gas law that includes the quantity of gas in a sample as well as the temperature, pressure, and volume of the sample. This law, known as the **ideal gas law**, is written as

$$PV = nRT \quad (6.9)$$

In this equation, P , V , and T are defined as they were in the gas laws given earlier. The symbol n stands for the number of moles of gas in the sample being used, and R is a constant known as the **universal gas constant**. The measured value for the volume of 1 mol of gas at STP allows R to be evaluated by substituting the values into Equation 6.9 after rearrangement to isolate R :

$$R = \frac{PV}{nT} = \frac{(1.00 \text{ atm})(22.4 \text{ L})}{(1 \text{ mol})(273 \text{ K})} = 0.0821 \frac{\text{L atm}}{\text{mol K}}$$

This value of R is the same for all gases under any conditions of temperature, pressure, and volume.

universal gas constant The constant that relates pressure, volume, temperature, and number of moles of gas in the ideal gas law.

Example 6.8

Use the ideal gas law to calculate the volume of 0.413 mol hydrogen gas at a temperature of 20°C and a pressure of 1200 torr.

Solution

To use the ideal gas law (Equation 6.9), it is necessary that all units match those of R . Thus, the temperature will have to be expressed in kelvins and the pressure in atmospheres:

$$K = ^\circ C + 273 = 20^\circ C + 273 = 293 \text{ K}$$

$$P = (1200 \text{ torr}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) = 1.58 \text{ atm}$$

Because volume is the desired quantity, we isolate it by dividing both sides of the ideal gas law by P :

$$\frac{PV}{P} = \frac{nRT}{P} \quad \text{or} \quad V = \frac{nRT}{P}$$

Substitution of quantities gives

$$V = \frac{(0.413 \text{ mol}) \left(0.0821 \frac{\text{L atm}}{\text{mol K}} \right) (293 \text{ K})}{(1.58 \text{ atm})} = 6.29 \text{ L}$$

Learning Check 6.7 A 2.15-mol sample of sulfur dioxide gas (SO_2) occupies a volume of 12.6 L at 30°C. What is the pressure of the gas in atm?

Because R is a constant for all gases, it follows that if any three of the quantities P , V , T , or n are known for a gas sample, the fourth quantity can be calculated by using Equation 6.9. An interesting application of this concept makes it possible to determine the molecular weights of gaseous substances. If the mass of a sample is known, the number of moles in the sample is the mass in grams divided by the molecular weight. This fact is represented by Equation 6.10, where n is the number of moles in a sample that has a mass in grams of m and a molecular weight of MW:

$$n = \frac{m}{\text{MW}} \quad (6.10)$$

When $\frac{m}{\text{MW}}$ is substituted for n in Equation 6.9, the result is

$$PV = \frac{mRT}{\text{MW}} \quad (6.11)$$

Example 6.9

A gas sample has a volume of 2.74 L, a mass of 16.12 g and is stored at a pressure of 4.80 atm at a temperature of 25°C. The gas might be CH₄, C₂H₆, or C₃H₁₀. Which gas is it?

Solution

The molecular weight of the gas is determined using Equation 6.11 and compared with the molecular weights of the three possibilities calculated from their formulas. Rearrangement of Equation 6.11 to isolate molecular weight gives

$$MW = \frac{mRT}{PV}$$

Substitution of the known quantities after conversion to proper units gives

$$MW = \frac{mRT}{PV} = \frac{(16.12 \text{ g}) \left(0.0821 \frac{\text{L atm}}{\text{mol K}} \right) (298 \text{ K})}{(4.80 \text{ atm})(2.74 \text{ L})} = 30.0 \text{ g/mol}$$

Thus, the molecular weight is 30.0 u. This matches the molecular weight of C₂H₆ calculated from atomic weights and the molecular formula.

Learning Check 6.8 A sample of unknown gas has a mass of 3.35 g and occupies 2.00 L at 1.21 atm and 27°C. What is the molecular weight of the gas? Is the gas H₂S, HBr, or NH₃?

The gas laws discussed in this chapter apply only to gases that are ideal, but interestingly, no ideal gases actually exist. If they did exist, ideal gases would behave exactly as predicted by the gas laws at all temperatures and pressures. Real gases deviate from the behavior predicted by the gas laws, but under normally encountered temperatures and pressures, the deviations are small for many real gases. This fact allows the gas laws to be used for real gases. Interparticle attractions tend to make gases behave less ideally. Thus, the gas laws work best for gases in which such forces are weak, that is, those made up of single atoms (the noble gases) or nonpolar molecules (O₂, N₂, etc.). Highly polar molecules such as water vapor, hydrogen chloride, and ammonia deviate significantly from ideal behavior.

6.9 Dalton's Law

Learning Objective

7. Do calculations based on Dalton's law.

John Dalton (1766–1844), an English schoolteacher, made a number of important contributions to chemistry. Some of his experiments led to the law of partial pressures, also called **Dalton's law**. According to this law, the total pressure exerted by a mixture of different gases kept at a constant volume and temperature is equal to the sum of the partial pressures of the gases in the mixture. The **partial pressure** of each gas in such mixtures is the pressure each gas would exert if it were confined alone under the same temperature and volume conditions as the mixture.

Imagine you have four identical gas containers, as shown in Figure 6.8. Place samples of three different gases (represented by Δ , \circ , and \square) into three of the containers, one to a container, and measure the pressure exerted by each sample. Then place all three samples into the fourth container and measure the total pressure (P_t) exerted. The result is a statement of Dalton's law:

$$P_t = P_{\Delta} + P_{\circ} + P_{\square} \quad (6.12)$$

where P_{Δ} , P_{\circ} , and P_{\square} are the partial pressures of gases Δ , \circ , and \square , respectively.

Dalton's law of partial pressures

The total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the gases in the mixture.

partial pressure The pressure an individual gas of a mixture would exert if it were in the container alone at the same temperature as the mixture.

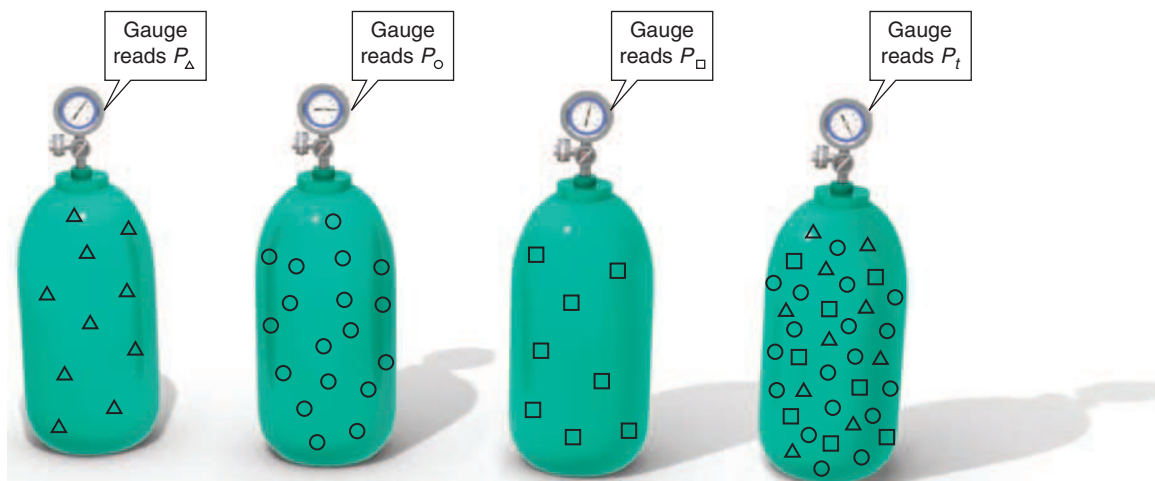


Figure 6.8 Dalton's law of partial pressures.

Example 6.10

A sample of air is collected when the atmospheric pressure is 742 torr. The partial pressures of nitrogen and oxygen in the sample are found to be 581 torr and 141 torr, respectively. Assume water vapor to be the only other gas present in the air sample, and calculate its partial pressure.

Solution

Dalton's law says $P_t = P_{O_2} + P_{N_2} + P_{H_2O}$. The total pressure of the sample is the atmospheric pressure of 742 torr. Therefore,

$$742 \text{ torr} = 141 \text{ torr} + 581 \text{ torr} + P_{H_2O}$$

and

$$P_{H_2O} = 742 - 141 - 581 = 20 \text{ torr}$$

Learning Check 6.9 A mixture is made of helium, nitrogen, and oxygen. Their partial pressures are, respectively, 310 torr, 0.200 atm, and 7.35 psi. What is the total pressure of the mixture in torr?

6.10 Graham's Law

Learning Objective

- Do calculations based on Graham's law.

Effusion and diffusion are processes by which gases move and mix. **Effusion** is the escape of a gas through a small hole in its container. **Diffusion** is the process in which two or more gases spontaneously intermingle when brought together. Even though the processes appear to be different, they are related, and both follow a law proposed in 1828 by Thomas Graham to describe effusion (see Figure 6.9). For two gases, represented by A and B , **Graham's law** is

$$\frac{\text{effusion rate } A}{\text{effusion rate } B} = \sqrt{\frac{\text{molecular mass of } B}{\text{molecular mass of } A}} \quad (6.13)$$

Example 6.11

Oxygen molecules weigh 16 times as much as hydrogen molecules. Which molecule will diffuse faster and how much faster?

effusion A process in which a gas escapes from a container through a small hole.

diffusion A process that causes gases to spontaneously intermingle when they are brought together.

Graham's law A mathematical expression that relates rates of effusion or diffusion of two gases to the masses of the molecules of the two gases.



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- 1 A balloon freshly filled with helium.



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- 2 The same balloon the next morning.

Figure 6.9 Graham's law in action. Would a balloon filled with hydrogen gas deflate more slowly or faster than the helium-filled balloon?

evaporation or vaporization An endothermic process in which a liquid is changed to a gas.

Figure 6.10 Endothermic and exothermic changes of state.

Solution

Applying Equation 6.13 but recognizing that diffusion follows the equation as well as effusion, we get

$$\frac{\text{rate H}_2}{\text{rate O}_2} = \sqrt{\frac{\text{mass O}_2}{\text{mass H}_2}} = \sqrt{\frac{32}{2}} = \sqrt{16} = 4$$

Therefore, we conclude that hydrogen will diffuse four times faster than oxygen.

► **Learning Check 6.10** Which will diffuse faster, He molecules or Ne molecules? How much faster?

6.11 Changes in State

Learning Objective

9. Classify changes in state as exothermic or endothermic.

Matter can be changed from one state into another by processes such as heating, cooling, or changing the pressure. Heating and cooling are the processes most often used, and a change in state that requires an input of heat is called endothermic, whereas one in which heat is given up (or removed) is called exothermic (see Section 5.8). (These terms come from the Greek *endo* = in and *exo* = out). Endothermic changes are those in which particles are moved farther apart as cohesive forces are being overcome, such as the change of a solid to a liquid or gas. Exothermic changes are those in the opposite direction. See

► Figure 6.10.

► **Learning Check 6.11** Classify the following processes as endothermic or exothermic:

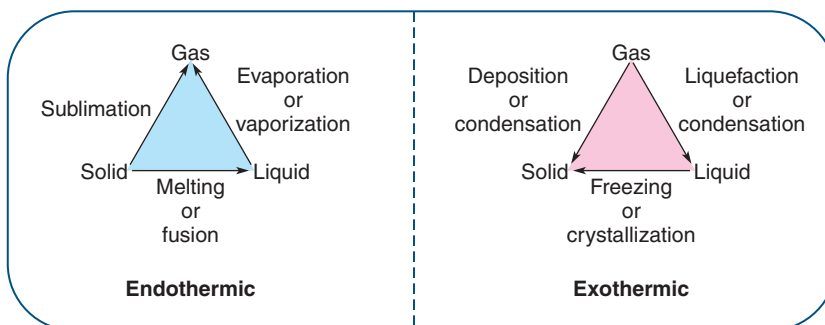
- Alcohol evaporates.
- Water freezes.
- Iron melts in a furnace.

6.12 Evaporation and Vapor Pressure

Learning Objective

10. Demonstrate an understanding of the concepts of vapor pressure and evaporation.

The evaporation of liquids is a familiar process. Water in a container will soon disappear (evaporate) if the container is left uncovered. **Evaporation**, or **vaporization**, is an endothermic process that takes place as a result of molecules leaving the surface of a liquid. The rate of evaporation depends on the temperature of the liquid and the surface area



from which the molecules can escape. Temperature is an important factor because it is related directly to the speed and kinetic energy of the molecules and hence to their ability to break away from the attractive forces present at the liquid surface.

Evaporating molecules carry significant amounts of kinetic energy away from the liquid, and as a result, the temperature of the remaining liquid will drop unless heat flows in from the surroundings. This principle is involved in all evaporative cooling processes, including evaporative coolers for homes, the cooling of the human body by perspiration, and the cooling of a panting dog by the evaporation of saliva from the mucous membranes of its mouth.

Compare evaporation in a closed container (▶ Figure 6.11) with that in an open container. Evaporation occurs in both containers, as indicated by a drop in liquid level. But, unlike that in an open container, the liquid level in the closed container eventually stops dropping and becomes constant.

What would explain this behavior? In a closed container the molecules of liquid that go into the vapor (gaseous) state are unable to move completely away from the liquid surface as they do in an open container. Instead, the vapor molecules are confined to a space immediately above the liquid, where they have many random collisions with the container walls, other vapor molecules, and the liquid surface. Occasionally, their collisions with the liquid result in condensation, and they are recaptured by the liquid. **Condensation** is an exothermic process in which a gas or vapor is converted to either a liquid or a solid. Thus, two processes—evaporation (escape) and condensation (recapture)—actually take place in the closed container. Initially, the rate of evaporation exceeds that of condensation, and the liquid level drops. However, the rates of the two processes eventually become equal, and the liquid level stops dropping because the number of molecules that escape in a given time is the same as the number recaptured.

A system in which two opposite processes take place at equal rates is said to be in equilibrium (see Chapter 8). Under the equilibrium conditions just described, the number of molecules in the vapor state remains constant. This constant number of molecules will exert a constant pressure on the liquid surface and the container walls. This pressure exerted by a vapor in equilibrium with a liquid is called the **vapor pressure** of the liquid. The magnitude of a vapor pressure depends on the nature of the liquid (molecular polarity, mass, etc.) and the temperature of the liquid. These dependencies are illustrated in ▶ Tables 6.4 and 6.5.

condensation An exothermic process in which a gas or vapor is changed to a liquid or solid.

vapor pressure The pressure exerted by vapor that is in equilibrium with its liquid.

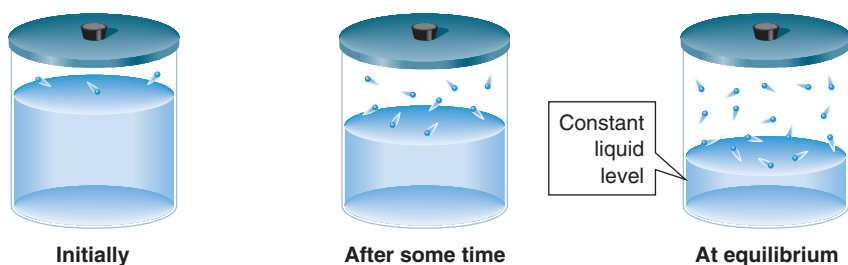


Figure 6.11 Liquid evaporation in a closed container. The drop in liquid level is greatly exaggerated for emphasis.

Table 6.4 The Vapor Pressure of Various Liquids at 20°C

Liquid	Molecular Weight (u)	Polarity	Vapor Pressure (torr)
pentane (C ₅ H ₁₂)	72	Nonpolar	414.5
hexane (C ₆ H ₁₄)	86	Nonpolar	113.9
heptane (C ₇ H ₁₆)	100	Nonpolar	37.2
ethanol (C ₂ H ₅ —OH)	46	Polar (hydrogen bonds)	43.9
1-propanol (C ₃ H ₇ —OH)	60	Polar (hydrogen bonds)	17.3
1-butanol (C ₄ H ₉ —OH)	74	Polar (hydrogen bonds)	7.1

Table 6.5 Vapor Pressure of Water at Various Temperatures

Temperature (°C)	Vapor Pressure (torr)
0	4.6
20	17.5
40	55.3
60	149.2
80	355.5
100	760.0

Chemistry Around Us 6.1

Sweating It Out



Even though the cosmetics industry sells millions of dollars worth of products each year to prevent it, sweating is as natural a process for the human body as is breathing. It is also an essential process that helps control body temperature. Because of hydrogen bonding between its molecules, liquid water has a surprisingly large heat of vaporization of 540 cal/g. This means that 540 calories of heat must be absorbed by each gram of water that changes from the liquid to the vapor state. When excess body heat is generated by metabolic activity in the body or by exposure to surroundings that are warmer than the body, sweat, a dilute solution that contains about 99% water, is actively released onto the surface of the skin by millions of sweat glands. At an air temperature of 20°C (68°F), an adult loses an average of about 100 mL of water daily through sweating. However, as the air temperature and degree of activity increase, the rate of sweating increases dramatically, and in some cases gets as high as 2 liters per hour.

If 1 liter (or 1000 g) of sweat evaporated per hour from an individual, 540 thousand cal of heat energy would be removed from that person's body during that hour. Usually, however, when sweat is produced in such abundance it does not all evaporate; a significant amount drips off or runs off the skin and does not contribute to the cooling process. The amount that evaporates also depends on the relative humidity of the surrounding air. Relative humidity is the percentage of water vapor present in the air compared to the maximum amount the air can hold at that temperature. For example, if the relative humidity is 70%, the

air already has in it 70% of the maximum amount of water vapor it can possibly hold. Such high-humidity air does not accept as much evaporated water as less humid air and therefore slows the evaporation process. Thus, a profusely sweating person on a hot, humid day is likely to be getting less-efficient body cooling than a person on a hot, dry day who shows only a slight amount of moisture on the skin.



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Sweat is a part of the body's cooling system.

The effect of molecular mass on vapor pressure is seen in both the pentane–heptane and ethanol–1-butanol series of compounds in Table 6.4. Within each series, the molecular polarities are the same for each member, but vapor pressure decreases as molecular weight increases. This shows the effect of stronger dispersion forces between heavier molecules. A comparison of pentane and 1-butanol shows the effects of polar attractions between molecules. Molecules of these liquids have similar molecular weights, but the hydrogen-bonded 1-butanol has a much lower vapor pressure.

The effect of increasing the kinetic energy of molecules by heating is clearly evident by the vapor pressure behavior of water shown in Table 6.5.

► **Learning Check 6.12** Decide which member of each of the following pairs of compounds would have the higher vapor pressure. Explain your choice in each case.

- a. Methyl alcohol (CH_3OH) and propyl alcohol ($\text{C}_3\text{H}_7\text{OH}$)
- b. Liquid helium (He) and liquid nitrogen (N_2)
- c. Liquid HF and liquid neon (Ne)

6.13 Boiling and the Boiling Point

Learning Objective

- 11.** Demonstrate an understanding of the process of boiling and the concept of boiling point.

As a liquid is heated, its vapor pressure increases, as shown for water in Table 6.5. If the liquid's temperature is increased enough, its vapor pressure will reach a value equal to that of the prevailing atmospheric pressure. Up to that temperature, all vaporization

Table 6.6 Variations in the Boiling Point of Water with Elevation

Location	Elevation (feet above sea level)	Boiling Point of Water (°C)
San Francisco, CA	Sea level	100.0
Salt Lake City, UT	4,390	95.6
Denver, CO	5,280	95.0
La Paz, Bolivia	12,795	91.4
Mount Everest	20,028	76.5

appears to take place at the liquid surface. However, when the vapor pressure becomes equal to atmospheric pressure, vaporization begins to occur beneath the surface as well. When bubbles of vapor form and rise rapidly to the surface, where the vapor escapes, the liquid is boiling. The **boiling point** of a liquid is the temperature at which the vapor pressure of the liquid is equal to the atmospheric pressure above the liquid. The **normal** or **standard boiling point** of a liquid is the temperature at which the vapor pressure is equal to 1 standard atmosphere (760 torr). Normal values were used in all examples of boiling points given earlier in this book.

Liquids boil at temperatures higher than their normal boiling points when external pressures are greater than 760 torr. When external pressures are less than 760 torr, liquids boil at temperatures below their normal boiling points. Thus, the boiling point of water fluctuates with changes in atmospheric pressure. Such fluctuations seldom exceed 2°C at a specific location, but there can be striking variations at different elevations, as shown by Table 6.6. (This is why cooking directions are sometimes different for different altitudes.)

The increase in boiling point caused by an increase in pressure is the principle used in the ordinary pressure cooker. Increasing the pressure inside the cooker causes the boiling point of the water in it to rise, as shown in Table 6.7. It then becomes possible to increase the temperature of the food-plus-water in the cooker above 100°C. Such an increase of just 10°C will make the food cook approximately twice as fast (see Figure 6.12).

boiling point The temperature at which the vapor pressure of a liquid is equal to the prevailing atmospheric pressure.

normal or standard boiling point The temperature at which the vapor pressure of a liquid is equal to 1 standard atmosphere (760 torr).

Table 6.7 The Boiling Point of Water in a Pressure Cooker

Pressure above Atmospheric		Boiling Point of Water (°C)
psi	torr	
5	259	108
10	517	116
15	776	121

6.14 Sublimation and Melting

Learning Objective

12. Demonstrate an understanding of the processes of sublimation and melting.

Solids, like liquids, have vapor pressures. Although the motion of particles is much more restricted in solids, particles at the surface can escape into the vapor state if they acquire sufficient energy. However, the strong cohesive forces characteristic of the solid state usually cause the vapor pressures of solids to be quite low.



Figure 6.12 A pressure cooker shortens the time required to cook food. A carrot cooks completely in boiling water (100°C) in 8 minutes. About how long would it take to cook in a pressure cooker that raised the boiling point of water to 110°C?

sublimation The endothermic process in which a solid is changed directly to a gas without first becoming a liquid.

melting point The temperature at which a solid changes to a liquid; the solid and liquid have the same vapor pressure.

decomposition A change in chemical composition that can result from heating.

As expected, vapor pressures of solids increase with temperature. When the vapor pressure of a solid is high enough to allow escaping molecules to go directly into the vapor state without passing through the liquid state, the process is called **sublimation** (see Figure 6.13). Sublimation is characteristic of materials such as solid carbon dioxide (dry ice) and naphthalene (moth crystals). Frozen water also sublimates under appropriate conditions. Wet laundry hung out in freezing weather eventually dries as the frozen water sublimates. Freeze drying, a technique based on this process, is used to remove water from materials that would be damaged by heating (e.g., freeze-dried foods).

Even though solids have vapor pressures, most pure substances in the solid state melt before appreciable sublimation takes place. Melting involves the breakdown of a rigid, orderly, solid structure into a mobile, disorderly liquid state. This collapse of the solid structure occurs at a characteristic temperature called the **melting point**. At the melting point, the kinetic energy of solid particles is large enough to partially overcome the strong cohesive forces holding the particles together, and the solid and liquid states have the same vapor pressure.

In some instances, solids cannot be changed into liquids, or liquids into gases, by heating. The atoms making up the molecules of some solids acquire enough kinetic energy on heating to cause bonds within the molecules to break before the solid (or liquid) can change into another state. This breaking of bonds within molecules changes the composition of the original substance. When this **decomposition** occurs, the original substance is said to have decomposed. This is why cotton and paper, when heated, char rather than melt.

6.15 Energy and the States of Matter

Learning Objective

- 13.** Do calculations based on energy changes that accompany heating, cooling, or changing the state of a substance.

A pure substance in the gaseous state contains more energy than in the liquid state, which in turn contains more energy than in the solid state. Before we look at this, note the following relationships. Kinetic energy, the energy of particle motion, is related to heat. In fact, temperature is a measurement of the average kinetic energy of the particles in a system. Potential energy, in contrast, is related to particle separation distances rather than motion. Thus, we conclude that an increase in temperature on adding heat corresponds to an increase in kinetic energy of the particles, whereas no increase in temperature on adding heat corresponds to an increase in the potential energy of the particles.

Now let's look at a system composed of 1 g of ice at an initial temperature of -20°C . Heat is added at a constant rate until the ice is converted into 1 g of steam at 120°C . The atmospheric pressure is assumed to be 760 torr throughout the experiment. The changes in the system take place in several steps, as shown in Active Figure 6.14.

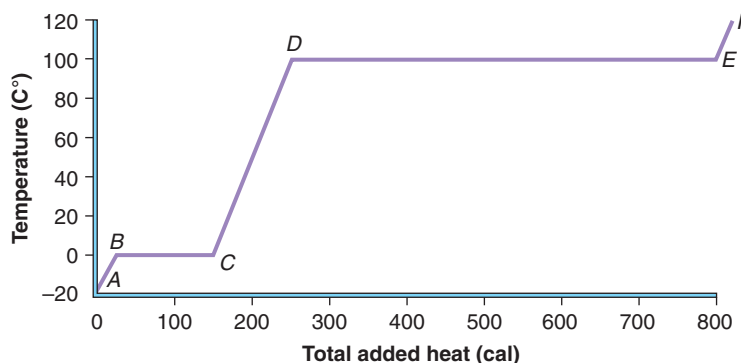


Figure 6.13 Solid CO_2 (left) and solid H_2O (right) both sublime. Contrast the endothermic processes involved when each is used in the most common way to keep things cold. Are the same processes involved?

Active Figure 6.14 The temperature behavior of a system during changes in state. Go to www.cengage.com/chemistry/seager or OWL to explore an interactive version of this figure.

Therapeutic Uses of Oxygen Gas



A steady supply of oxygen is essential for the human body to function properly. The most common source of this gas is inhaled air, in which the partial pressure of oxygen is about 160 torr. In a healthy individual, this partial pressure is high enough to allow sufficient oxygen needed for body processes to be transported into the blood and distributed throughout the body. Patients suffering from a lung disease, such as pneumonia or emphysema, often cannot transport sufficient oxygen to the blood from the air they breathe unless the partial pressure of oxygen in the air is increased. This is done by mixing an appropriate amount of oxygen with the air by using an oxygen mask or nasal cannula.

Oxygen at very high partial pressures is used in other clinical applications based on a technique called *hyperbaric oxygenation*. In one application, patients infected by anaerobic bacteria, such as those that cause tetanus and gangrene, are placed in a hyperbaric chamber in which the partial pressure of oxygen is 3 to 4 standard atmospheres (2.2×10^3 to 3.0×10^3 torr). Because of the high partial pressure, body tissues pick up large amounts of oxygen, and the bacteria are killed.

Hyperbaric oxygenation may also be used to treat other abnormal conditions or injuries, such as certain heart disorders, carbon monoxide

poisoning, crush injuries, certain hard-to-treat bone infections, smoke inhalation, near-drowning, asphyxia, and burns.



Hyperbaric chambers must be strongly built to resist significant internal gas pressure.

The solid is first heated from -20°C to the melting point of 0°C (line *AB*). The temperature increase indicates that most of the added heat causes an increase in the kinetic energy of the molecules. Along line *BC*, the temperature remains constant at 0°C while the solid melts. The constant temperature during melting reveals that the added heat has increased the potential energy of the molecules without increasing their kinetic energy; the molecules are moved farther apart, but their motion is not increased. The addition of more heat warms the liquid water from 0°C to the normal boiling point of 100°C (line *CD*). At 100°C , another change of state occurs as heat is added, and the liquid is converted into vapor (steam) at 100°C (line *DE*). The constant temperature of this process again indicates an increase in potential energy. Line *EF* represents heating the steam from 100°C to 120°C by adding more heat.

The addition of heat to this system resulted in two obviously different results: The temperature of water in a specific state was increased, or the water was changed from one state to another at constant temperature. The amount of heat required to change the temperature of a specified amount of a substance by 1°C is called the **specific heat** of the substance. In scientific work, this is often given in units of calories or joules (J) per gram degree. Thus, the specific heat of a substance is the number of calories or joules required to raise the temperature of 1 g of the substance by 1°C . (NOTE: $1 \text{ cal} = 4.184 \text{ J}$.) The specific heat is related to the amount of heat required to increase the temperature of a sample of substance by Equation 6.14.

$$\text{Heat} = (\text{sample mass})(\text{specific heat})(\text{temp. change}) \quad (6.14)$$

Specific heats for a number of substances in various states are listed in Table 6.8. A substance with a high specific heat is capable of absorbing more heat with a small temperature change than substances with lower specific heats. Thus, substances to be used as heat transporters (e.g., in cooling and heating systems) should have high specific heats—note the value for liquid water.

Example 6.12

You notice that your car is running hot on a summer day. Someone tells you to drain out the ethylene glycol antifreeze and replace it with water. Will this allow the engine to run cooler?

specific heat The amount of heat energy required to raise the temperature of exactly 1 g of a substance by exactly 1°C .

Table 6.8 Specific Heats for Selected Substances

Substance and State	Specific Heat	
	cal/g Degree	J/g Degree
Aluminum (solid)	0.24	1.0
Copper (solid)	0.093	0.39
Ethylene glycol (liquid)	0.57	2.4
Helium (gas)	1.25	5.23
Hydrogen (gas)	3.39	14.2
Lead (solid)	0.031	0.13
Mercury (liquid)	0.033	0.14
Nitrogen (gas)	0.25	1.1
Oxygen (gas)	0.22	0.92
Sodium (solid)	0.29	1.2
Sodium (liquid)	0.32	1.3
Water (solid)	0.51	2.1
Water (liquid)	1.00	4.18
Water (gas)	0.48	2.0

Solution

The engine will run cooler because a given mass of water has a greater ability to carry heat from the engine to the radiator than does an equal mass of ethylene glycol. The coolant in your car is a mixture of ethylene glycol and water, but to simplify the following comparison, let us imagine it is pure ethylene glycol. We calculate the amount of heat absorbed by 1000 g each of pure ethylene glycol and pure water as the temperature changes from 20°C to 80°C.

$$\text{Heat absorbed} = (\text{mass})(\text{specific heat})(\text{temp. change})$$

$$\begin{aligned}\text{ethylene glycol:} \quad \text{Heat absorbed} &= (1000 \text{ g})\left(\frac{0.57 \text{ cal}}{\text{g}^\circ\text{C}}\right)(60^\circ\text{C}) \\ &= 34,200 \text{ cal} = 34.2 \text{ kcal}\end{aligned}$$

$$\begin{aligned}\text{water:} \quad \text{Heat absorbed} &= (1000 \text{ g})\left(\frac{1.00 \text{ cal}}{\text{g}^\circ\text{C}}\right)(60^\circ\text{C}) \\ &= 60,000 \text{ cal} = 60.0 \text{ kcal}\end{aligned}$$

Thus, the same amount of water will absorb (and transport) nearly twice as much heat for the same temperature increase.

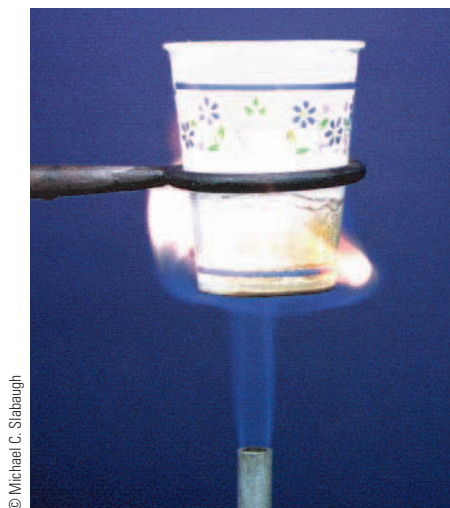
► **Learning Check 6.13** Some nuclear reactors are cooled by gases. Calculate the number of calories that 1.00 kg of helium gas will absorb when it is heated from 25°C to 700°C. See Table 6.8 for the specific heat of He.

heat of fusion The amount of heat energy required to melt exactly 1 g of a solid substance at constant temperature.

heat of vaporization The amount of heat energy required to vaporize exactly 1 g of a liquid substance at constant temperature.

The amount of heat required to change the state of 1 g of a substance at constant temperature is called the **heat of fusion** (for melting) and the **heat of vaporization** (for boiling). The units used for these quantities are just calories or joules per gram because no temperature changes are involved. These heats represent the amount of energy required to change 1 g of a substance to the liquid or vapor state at the characteristic melting or boiling point. The heats of fusion and vaporization for water are 80 and 540 cal/g, respectively. This explains why a burn caused by steam at 100°C

is more severe than one caused by water at 100°C. Vaporization has added 540 cal to each gram of steam, and each gram will release these 540 cal when it condenses on the skin. Liquid water at 100°C would not have this extra heat with which to burn the skin (see Figure 6.15).



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- 1 A paper cup filled with water does not reach the ignition temperature when heated by a burner, but the water boils.



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- 2 An empty paper cup burns when heated by a burner because the heat from the burner increases the temperature of the cup to the ignition point.

Figure 6.15 Water can be boiled in a paper cup. Explain why heat from the burner does not increase the temperature of the water-containing cup to the ignition temperature.

Study Skills 6.1 Which Gas Law to Use

For many students, the biggest challenge of this chapter is solving problems using the gas laws. Once you recognize that you are faced with a gas law problem, you must decide which of the six gas laws will work to solve the problem. One aid to selecting the appropriate law is to look for key words, phrases, or ideas that are often associated with specific laws. Some of these are given here:

Gas Law	Equation	Key
Boyle's law	$PV = k$	T is constant
Charles's law	$\frac{V}{T} = k'$	P is constant
Combined gas law	$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$	P , V , and T all change
Dalton's law	$P_t = P_{\Delta} + P_{\text{O}} + P_{\text{□}}$	Two or more different gases
Graham's law	$\frac{\text{effusion rate } A}{\text{effusion rate } B} = \sqrt{\frac{\text{molecular mass of } B}{\text{molecular mass of } A}}$	Effusion and diffusion
Ideal gas law	$PV = nRT$	Moles of gas

For example, if you see the key word *diffusion*, it is likely that you are dealing with a Graham's law problem.

The first three gas laws (Boyle's, Charles's, and the combined) are very similar in that they all use the symbols P , V , and T . If you have narrowed down a gas law problem to one of these three, a simple approach is to use the combined gas law. It works in all three cases. If T is constant,

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

simplifies to $P_i V_i = P_f V_f$, a form of Boyle's law. If P is constant, it simplifies to

$$\frac{V_i}{T_i} = \frac{V_f}{T_f}$$

a form of Charles's law. If V is constant, the combined law becomes

$$\frac{P_i}{T_i} = \frac{P_f}{T_f}$$

an equation that is not named but is useful for certain problems.

A final point to remember is that temperatures must be expressed in kelvins to get correct answers using any of the gas laws that involve temperature.

Example 6.13

Calculate the heat released when 5.0 kg of steam at 120°C condenses to water at 100°C in a radiator of a steam heating system.

Solution

Consider the process as taking place in two steps. The steam must cool from 120°C to 100°C and then condense to liquid water at 100°C. When the steam cools to 100°C,

$$\begin{aligned}\text{Heat released} &= (\text{mass})(\text{specific heat})(\text{temp. change}) \\ &= (5.0 \times 10^3 \text{ g})\left(\frac{0.48 \text{ cal}}{\text{g}^\circ\text{C}}\right)(20^\circ\text{C}) \\ &= 4.8 \times 10^4 \text{ cal} = 48 \text{ kcal}\end{aligned}$$

When the steam condenses to liquid water at 100°C,

$$\begin{aligned}\text{Heat released} &= (\text{mass})(\text{heat of vaporization}) \\ &= (5.0 \times 10^3 \text{ g})\left(\frac{540 \text{ cal}}{\text{g}}\right) \\ &= 2.7 \times 10^6 \text{ cal} = 2.7 \times 10^3 \text{ kcal}\end{aligned}$$

Note that the heat of vaporization was used even though the water was changing from the vapor to the liquid state. The only difference between vaporization and condensation is the direction of heat flow; the amount of heat involved remains the same for a specific quantity of material. (Accordingly, 1 g of liquid water will release 80 cal when it freezes.)

These results make it clear that most of the transported heat (98%) was carried in the form of potential energy, which was released when the steam condensed.

► **Learning Check 6.14** Suppose the radiator of your car overheats and begins to boil. Calculate the number of calories absorbed by 5.00 kg of water (about 1 gallon) as it boils and changes to steam.

Concept Summary

Observed Properties of Matter. Matter in the solid, liquid, or gaseous state shows differences in physical properties such as density, shape, compressibility, and thermal expansion.

Objective 1, Exercise 6.2

The Kinetic Molecular Theory of Matter. Much of the behavior of matter in different states can be explained by the kinetic molecular theory, according to which all matter is composed of tiny molecules that are in constant motion and are attracted or repelled by each other.

Objective 2, Exercise 6.8

The Solid State. In the solid state, cohesive forces between particles of matter are stronger than disruptive forces. As a result, the particles of solids are held in rigid three-dimensional lattices in which the particle's kinetic energy takes the form of vibrations about each lattice site.

Objective 3, Exercises 6.12 and 6.16

The Liquid State. In the liquid state, cohesive forces between particles slightly dominate disruptive forces. As a result, particles of liquids are randomly arranged but relatively close to each other and are in constant random motion, sliding freely over each other but without enough kinetic energy to become separated.

Objective 3, Exercises 6.12 and 6.16

The Gaseous State. In the gaseous state, disruptive forces dominate and particles move randomly, essentially independent of each other. Under ordinary pressure, the particles are separated from each other by relatively large distances except when they collide.

Objective 3, Exercises 6.12 and 6.16

The Gas Laws. Mathematical relationships, called gas laws, describe the observed behavior of gases when they are mixed, subjected to pressure or temperature changes, or allowed to diffuse. When these relationships are used, it is necessary to express the volume and pressure in consistent units and the temperature in kelvins.

Objective 4, Exercises 6.20 and 6.22

Pressure, Temperature, and Volume Relationships. Gas laws discovered by Robert Boyle and Jacques Charles led to the development of the combined gas law. This law allows calculations to be made that relate temperature, pressure, and volume changes for gases.

Objective 5, Exercises 6.24, 6.32, and 6.34

The Ideal Gas Law. The application of a gas law discovered by Amadeo Avogadro to the combined gas law led to the ideal gas law, which allows calculations to be made that account for the number of moles of gas in a sample.

Objective 6, Exercise 6.46

Dalton's Law. John Dalton discovered experimentally that the total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the individual gases in the mixture.

Objective 7, Exercise 6.58

Graham's Law. Thomas Graham proposed a relationship that mathematically relates the rate of effusion or diffusion of a gas to the mass of the gas molecules:

$$\frac{\text{effusion rate } A}{\text{effusion rate } B} = \sqrt{\frac{\text{molecular mass of } B}{\text{molecular mass of } A}}$$

Objective 8, Exercise 6.60

Changes in State. Most matter can be changed from one state to another by heating, cooling, or changing pressure. State changes that give up heat are called exothermic, and those that absorb heat are called endothermic.

Objective 9, Exercise 6.64

Evaporation and Vapor Pressure. The evaporation of a liquid is an endothermic process and as a result is involved in many cooling processes. In a closed container, evaporation takes place only until the rate of escape of molecules from the liquid is equal to the rate at which they return to the liquid. The pressure exerted by the vapor, which is in equilibrium with the liquid, is called the vapor pressure

of the liquid. Liquid vapor pressures increase as the liquid temperature increases.

Objective 10, Exercise 6.67

Boiling and the Boiling Point. At the boiling point of a liquid, its vapor pressure equals the prevailing atmospheric pressure, and bubbles of vapor form within the liquid and rise to the surface as the liquid boils. The boiling point of a liquid changes as the prevailing atmospheric pressure changes.

Objective 11, Exercise 6.70

Sublimation and Melting. Solids, like liquids, have vapor pressures that increase with temperature. Some solids have high enough vapor pressures to allow them to change to vapor without first becoming a liquid, a process called sublimation. Most solids change to the liquid state before they change to the vapor state. The temperature at which solids change to liquids is called the melting point.

Objective 12, Exercise 6.74

Energy and the States of Matter. Energy is absorbed or released when matter is changed in temperature or changed from one state to another. The amount of heat energy required to produce temperature changes is called the specific heat of the matter involved. For phase changes, the amount of heat required is called the heat of fusion, or vaporization.

Objective 13, Exercises 6.76 and 6.78

Key Terms and Concepts


Absolute zero (6.6)	Disruptive force (6.2)	Potential energy (6.2)
Avogadro's law (6.8)	Effusion (6.10)	Pressure (6.6)
Boiling point (6.13)	Evaporation or vaporization (6.12)	Shape (6.1)
Boyle's law (6.7)	Gas law (6.6)	Specific heat (6.15)
Charles's law (6.7)	Graham's law (6.10)	Standard atmosphere (6.6)
Cohesive force (6.2)	Heat of fusion (6.15)	Standard conditions (STP) (6.8)
Combined gas law (6.7)	Heat of vaporization (6.15)	Sublimation (6.14)
Compressibility (6.1)	Ideal gas law (6.8)	Thermal expansion (6.1)
Condensation (6.12)	Kinetic energy (6.2)	Torr (6.6)
Dalton's law of partial pressures (6.9)	Melting point (6.14)	Universal gas constant (6.8)
Decomposition (6.14)	Normal or standard boiling point (6.13)	Vapor pressure (6.12)
Diffusion (6.10)	Partial pressure (6.9)	

Key Equations

1. Calculation of volume from mass and density (Section 6.1):	$V = \frac{m}{d}$	Equation 6.1
2. Calculation of kinetic energy of particles in motion (Section 6.2):	$KE = \frac{1}{2} mv^2$	Equation 6.2
3. Boyle's law (Section 6.7):	$P = \frac{k}{V}$	Equation 6.3
	$PV = k$	Equation 6.4
4. Charles's law (Section 6.7):	$V = k'T$	Equation 6.5
	$\frac{V}{T} = k'$	Equation 6.6

5. Combined gas law (Section 6.7):	$\frac{PV}{T} = k''$	Equation 6.7
	$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$	Equation 6.8
6. Ideal gas law (Section 6.8):	$PV = nRT$	Equation 6.9
7. Molecular weight determination (Section 6.8):	$PV = \frac{mRT}{\text{MW}}$	Equation 6.11
8. Dalton's law (Section 6.9):	$P_t = P_{\Delta} + P_{\circ} + P_{\square}$	Equation 6.12
9. Graham's law of effusion (Section 6.10):	$\frac{\text{effusion rate } A}{\text{effusion rate } B} = \sqrt{\frac{\text{molecular mass of } B}{\text{molecular mass of } A}}$	Equation 6.13
10. Heat calculation (Section 6.15):	Heat = (sample mass)(specific heat)(temp. change)	Equation 6.14

Exercises

 **OWL** Interactive versions of these problems are assignable in OWL.

Even-numbered exercises are answered in Appendix B.

Blue-numbered exercises are more challenging.

Observed Properties of Matter (Section 6.1)

- 6.1 Calculate the volume of 125 g of the following liquids:
 - a. Acetone ($d = 0.792 \text{ g/mL}$)
 - b. Olive oil ($d = 0.918 \text{ g/mL}$)
 - c. Chloroform ($d = 1.49 \text{ g/mL}$)
- 6.2 Calculate the volume of 125 g of the following liquids:
 - a. Sea water ($d = 1.03 \text{ g/mL}$)
 - b. Methyl alcohol ($d = 0.792 \text{ g/mL}$)
 - c. Concentrated sulfuric acid ($d = 1.84 \text{ g/mL}$)
- 6.3 Copper metal has a density of 8.92 g/cm^3 at 20.0°C and 8.83 g/cm^3 at 100.0°C . Calculate the change in volume that occurs when a 10.0-cm^3 piece of copper is heated from 20.0°C to 100.0°C .
- 6.4 Liquid water has a density of 1.00 g/mL at 10.0°C and 0.996 g/mL at 30.0°C . Calculate the change in volume that occurs when 500 mL of water is heated from 10.0°C to 30.0°C .
- 6.5 Gallium metal melts at 29.8°C . At the melting point, the density of the solid is 5.90 g/mL , and that of the liquid is 6.10 g/mL .
 - a. Does solid gallium expand or contract when it is melted? Explain.
 - b. What is the change in volume when $5.00 \text{ mL (cm}^3\text{)}$ of solid gallium is melted?
- 6.6 A 1.50-L rubber balloon is filled with carbon dioxide gas at a temperature of 0.00°C and a pressure of 1.00 atm . The density of the carbon dioxide gas under these conditions is 1.98 g/L .
 - a. Will the density of the carbon dioxide gas increase or decrease when the balloon is heated?
 - b. At 50.0°C , the balloon has a volume of 1.78 L . Calculate the carbon dioxide density at this temperature.

The Kinetic Molecular Theory of Matter (Section 6.2)

- 6.7 Describe the changes in form of energy (kinetic changes to potential, etc.) that occur for the energy of a rock dropped to the ground from a cliff. What form or forms do you suppose the energy takes when the rock hits the ground?
- 6.8 Suppose a toy ball is thrown into the air such that it goes straight up, then falls and is caught by the person who threw it. Describe the changes in the form of energy that occur for the ball from the time it is thrown until it is caught.
- 6.9 Suppose a 180-lb (81.8-kg) halfback running at a speed of 8.0 m/s collides head-on with a 260-lb (118.2-kg) tackle running at 3.0 m/s . Which one will be pushed back? That is, which one has more kinetic energy? If you're not familiar with football, check with someone who is for definition of terms.
- 6.10 At 25.0°C , He molecules (He) have an average velocity of $1.26 \times 10^5 \text{ cm/s}$, and methane molecules (CH_4) have an average velocity of $6.30 \times 10^4 \text{ cm/s}$. Calculate the kinetic energy of each type of molecule at 25.0°C and determine which is greater. Express molecular masses in u for this calculation.
- 6.11 Which have the greater kinetic energy, hydrogen molecules traveling with a velocity of $2v$, or helium molecules traveling with a velocity of v ? Express molecular masses in u.

The Solid, Liquid, and Gaseous States (Sections 6.3–6.5)

- 6.12 Explain each of the following observations using the kinetic molecular theory of matter:
 - a. A liquid takes the shape, but not necessarily the volume, of its container.
 - b. Solids and liquids are practically incompressible.
 - c. A gas always exerts uniform pressure on all walls of its container.

- 6.13** Explain each of the following observations using the kinetic molecular theory of matter:
- Gases have low densities.
 - The densities of a substance in the solid and liquid states are nearly identical.
 - Solids, liquids, and gases all expand when heated.
- 6.14** Discuss differences in kinetic and potential energy of the constituent particles for a substance in the solid, liquid, and gaseous states.
- 6.15** The following statements are best associated with the solid, liquid, or gaseous states of matter. Match the statements to the appropriate state of matter.
- This state is characterized by the lowest density of the three.
 - This state is characterized by an indefinite shape and a high density.
 - In this state, disruptive forces prevail over cohesive forces.
 - In this state, cohesive forces are most dominant.
- 6.16** The following statements are best associated with the solid, liquid, or gaseous states of matter. Match the statements to the appropriate state of matter.
- Temperature changes influence the volume of this state substantially.
 - In this state, constituent particles are less free to move about than in other states.
 - Pressure changes influence the volume of this state more than that of the other two states.
 - This state is characterized by an indefinite shape and a low density.

The Gas Laws (Section 6.6)

- 6.17** What is a gas law?
- 6.18** A weather reporter on TV reports the barometer pressure as 28.6 inches of mercury. Calculate this pressure in the following units:
- atm
 - torr
 - psi
 - bars
- 6.19** The pressure of a gas sample is recorded as 615 torr. Calculate this pressure in the following units:
- atm
 - in. Hg
 - psi
 - bars
- 6.20** An engineer reads the pressure gauge of a boiler as 210 psi. Calculate this pressure in the following units:
- atm
 - bars
 - mmHg
 - in. Hg

- 6.21** A chemist reads a pressure from a manometer attached to an experiment as 17.6 cmHg. Calculate this pressure in the following units:
- atm
 - mmHg
 - torr
 - psi
- 6.22** Convert each of the following temperatures from the unit given to the unit indicated:
- The melting point of potassium metal, 63.7°C, to kelvins.
 - The freezing point of liquid hydrogen, 14.1 K, to degrees Celsius.
 - The boiling point of liquid helium, -268.9°C, to kelvins.
- 6.23** Convert each of the following temperatures from the unit given to the unit indicated:
- The melting point of gold, 1337.4 K, to degrees Celsius.
 - The melting point of tungsten, 3410°C, to kelvins.
 - The melting point of tin, 505 K, to degrees Celsius.

Pressure, Temperature, and Volume Relationships (Section 6.7)

- 6.24** Use the combined gas law (Equation 6.8) to calculate the unknown quantity for each gas sample described in the following table.

	Sample		
	A	B	C
P_i	1.50 atm	2.35 atm	9.86 atm
V_i	2.00 L	1.97 L	11.7 L
T_i	300 K	293 K	500 K
P_f	?	1.09 atm	5.14 atm
V_f	3.00 L	?	9.90 L
T_f	450 K	310 K	?

- 6.25** A 200-mL sample of oxygen gas is collected at 26.0°C and a pressure of 690 torr. What volume will the gas occupy at STP (0°C and 760 torr)?
- 6.26** A 200-mL sample of nitrogen gas is collected at 45.0°C and a pressure of 610 torr. What volume will the gas occupy at STP (0°C and 760 torr)?
- 6.27** A 3.00-L sample of helium at 0.00°C and 1.00 atm is compressed into a 0.50-L cylinder. What pressure will the gas exert in the cylinder at 50°C?
- 6.28** A 2.50-L sample of neon at 0.00°C and 1.00 atm is compressed into a 0.75-L cylinder. What pressure will the gas exert in the cylinder at 30°C?
- 6.29** What volume (in liters) of air measured at 1.00 atm would have to be put into a bicycle tire with a 1.00-L volume if the pressure in the bike tire is to be 65.0 psi? Assume the temperature of the gas remains constant.
- 6.30** What volume (in liters) of air measured at 1.00 atm would have to be put into a car tire with a volume of 14.5 L if the pressure in the car tire is to be 32.0 psi? Assume the temperature of the gas remains constant.

- 6.31** A sample of gas has a volume of 500 mL at a pressure of 640 torr. What volume will the gas occupy at the same temperature but at the standard atmospheric pressure, 760 torr?
- 6.32** A sample of gas has a volume of 750 mL at a pressure of 700 torr. What volume will the gas occupy at the same temperature but at standard atmospheric pressure, 760 torr?
- 6.33** A 3.0-L sample of gas at 1.0 atm and 0.0°C is heated to 85°C. Calculate the gas volume at the higher temperature if the pressure remains at 1.0 atm.
- 6.34** A 3.8-L sample of gas at 1.0 atm and 20°C is heated to 75°C. Calculate the gas volume at the higher temperature if the pressure remains constant at 1.0 atm.
- 6.35** A sample of gas has a volume of 350 mL at 27°C. The gas is heated at a constant pressure until the volume is 500 mL. What is the new temperature of the gas in degrees Celsius?
- 6.36** What volume of gas at 120°C must be cooled to 35°C if the gas volume at constant pressure and 35°C is to be 1.5 L?
- 6.37** A 5.00-L gas sample is collected at a temperature and pressure of 27.0°C and 1.20 atm. The gas is to be transferred to a 3.00-L container at a pressure of 1.00 atm. What must the Celsius temperature of the gas in the 3.00-L container be?
- 6.38** A 2500-L sample of oxygen gas is produced at 1.00 atm pressure. It is to be compressed and stored in a 20.0-L steel cylinder. Assume it is produced and stored at the same temperature and calculate the pressure of the oxygen in the cylinder.
- 6.39** A steel tank with a volume of 6.25 L is full of gas at a pressure of 2.30 atm. What volume would the gas occupy at a pressure of 0.250 atm if its temperature did not change?
- 6.40** A helium balloon was partially filled with 8000 ft³ of helium when the atmospheric pressure was 0.98 atm and the temperature was 23°C. The balloon rose to an altitude where the atmospheric pressure was 400 torr and the temperature was 5.3°C. What volume did the helium occupy at this altitude?
- 6.41** You have a 1.50-L balloon full of air at 30°C. To what Celsius temperature would you have to heat the balloon to double its volume if the pressure remained unchanged?
- 6.42** A gas occupies 250 mL at a pressure of 2.10 atm. What volume would it occupy at the same temperature and a pressure of 60.0 kPa?
- 6.43** What minimum pressure would a 250-mL aerosol can have to withstand if it were to contain 2.00 L of gas measured at 700 torr? Assume constant temperature?
- 6.44** A 2.00-L sample of nitrogen gas at 760 torr and 0.0°C weighs 2.50 g. The pressure on the gas is increased to 3.00 atm at 0.0°C. Calculate the gas density at the new pressure in grams per liter.

The Ideal Gas Law (Section 6.8)

- 6.45** Use the ideal gas law and calculate the following:
- The pressure exerted by 2.00 mol of oxygen confined to a volume of 500 mL at 20.0°C.
 - The volume of hydrogen gas in a steel cylinder if 0.525 mol of the gas exerts a pressure of 3.00 atm at a temperature of 10.0°C.
 - The temperature (in degrees Celsius) of a nitrogen gas sample that has a volume of 2.50 L and a pressure of 300 torr and contains 0.100 mol.

- 6.46** Use the ideal gas law, and calculate the following:

- The number of moles of argon in a gas sample that occupies a volume of 400 mL at a temperature of 90.0°C and has a pressure of 735 torr.
 - The pressure exerted by 0.738 mol of hydrogen gas confined to a volume of 2.60 L at 45°C.
 - The volume of a tank of nitrogen if 1.75 mol of the gas exerts a pressure of 4.32 atm at 25°C.
- 6.47** Suppose 0.156 mol of SO₂ gas is compressed into a 0.750-L steel cylinder at a temperature of 27°C. What pressure in atmospheres is exerted by the gas?
- 6.48** Suppose 10.0 g of sulfur dioxide gas (SO₂) is compressed into a 0.750-L steel cylinder at a temperature of 27°C. What pressure does the compressed gas exert on the walls of the cylinder?
- 6.49** Calculate the volume occupied by 8.75 g of oxygen gas (O₂) at a pressure of 0.890 atm and a temperature of 35.0°C.
- 6.50** The pressure gauge of a steel cylinder of methane gas (CH₄) reads 380 psi. The cylinder has a volume of 0.500 L and is at a temperature of 30.0°C. How many grams of methane does the cylinder contain?
- 6.51** Suppose 10.0 g of dry ice (solid CO₂) was placed in an empty 400-mL steel cylinder. What pressure would develop if all the solid sublimed at a temperature of 35.0°C?
- 6.52** An experimental chamber has a volume of 60 L. How many moles of oxygen gas will be required to fill the chamber at STP?
- 6.53** How many molecules of nitrogen gas (N₂) are present in a sample that fills a 10.0-L tank at STP?
- 6.54** A sample of gaseous methyl ether has a mass of 8.12 g and occupies a volume of 3.96 L at STP. What is the molecular weight of methyl ether?
- 6.55** A sample of a gaseous nitrogen oxide is found to weigh 0.525 g. The sample has a volume of 300 mL at a pressure of 708 torr and a temperature of 25.7°C. Is the gas NO or NO₂?
- 6.56** A sample of gas weighs 0.176 g and has a volume of 114.0 mL at a pressure and temperature of 640 torr and 20°C. Determine the molecular weight of the gas, and identify it as CO, CO₂, or O₂.
- 6.57** A 2.00-g sample of gas has a volume of 1.12 L at STP. Calculate its molecular weight and identify it as He, Ne, or Ar.

Dalton's Law (Section 6.9)

- 6.58** A steel cylinder contains a mixture of nitrogen, oxygen, and carbon dioxide gases. The total pressure in the tank is 1800 torr. The pressure exerted by the nitrogen and oxygen is 750 torr and 810 torr, respectively. What is the partial pressure of CO₂ in the mixture?
- 6.59** A 250-mL sample of oxygen gas is collected by water displacement. As a result, the oxygen is saturated with water vapor. The partial pressure of water vapor at the prevailing temperature is 22 torr. Calculate the partial pressure of the oxygen if the total pressure of the sample is 720 torr.

Graham's Law (Section 6.10)

- 6.60** Hydrogen gas (H₂) is found to diffuse approximately four times as fast as oxygen gas (O₂). Using this information, determine how the masses of hydrogen molecules and oxygen molecules compare. How do they compare based on information in the periodic table?

- 6.61** The mass of a bromine molecule is 160 u, and the mass of an argon molecule is 40 u. Compare the rates at which these gases will diffuse.
- 6.62** Two identical rubber balloons were filled with gas—one with helium and the other with nitrogen. After a time, it was noted that one of the balloons appeared to be going “flat.” Which one do you think it was? Explain.
- 6.63** Assume the balloon in Exercise 6.62 that went flat first showed signs of “flatness” 12 hours after it was filled. How long would it take for the other balloon to begin to show signs of going flat?

Changes in State (Section 6.11)

- 6.64** Classify each of the following processes as endothermic or exothermic:
- Condensation
 - Liquefaction
 - Boiling
- 6.65** Classify each of the following processes as endothermic or exothermic:
- Freezing
 - Sublimation
 - Vaporization
- 6.66** Discuss what is meant by a change in state.

Evaporation and Vapor Pressure (Section 6.12)

- 6.67** The following are all nonpolar liquid hydrocarbon compounds derived from petroleum: butane (C_4H_{10}), pentane (C_5H_{12}), hexane (C_6H_{14}), and heptane (C_7H_{16}). Arrange these compounds in order of increasing vapor pressure (lowest first, highest last) and explain how you arrived at your answer.
- 6.68** Methylene chloride (CH_2Cl_2) was used at one time as a local anesthetic by dentists. It was sprayed onto the area to be anesthetized. Propose an explanation for how it worked.
- 6.69** Suppose a drop of methyl ether ($\text{C}_2\text{H}_6\text{O}$) was put on the back of one of your hands and a drop of ethyl ether ($\text{C}_4\text{H}_{10}\text{O}$) was put on your other hand. Propose a way you could tell which compound was which without smelling them.

Boiling and The Boiling Point (Section 6.13)

- 6.70** Each of two glass containers contains a clear, colorless, odorless liquid that has been heated until it is boiling. One liquid is water (H_2O) and the other is ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$). Explain how you could make one measurement of each boiling liquid, using the same device, and tell which liquid was which.
- 6.71** Suppose a liquid in an open container was heated to a temperature just 1 or 2 degrees below its boiling point, then insulated so it stayed at that temperature. Describe how the liquid would behave (what you would see happen) if the hot sample was suspended beneath a helium balloon and taken rapidly to higher altitudes.
- 6.72** Suppose you were on top of Mount Everest and wanted to cook a potato as quickly as possible. You left your microwave oven at home, so you could either boil the potato in water or throw it into a campfire. Explain which method you would use and why.

Sublimation and Melting (Section 6.14)

- 6.73** List three common substances that will sublime.
- 6.74** Solid iodine readily sublimates without melting when moderately heated. The hot vapor will condense back to the solid state when it cools. Describe a method that could be used to obtain pure solid iodine from a mixture of solid iodine and sand. Explain your reasoning.
- 6.75** A mixture was made of pure water and ice. The mixture was allowed to come to a constant temperature of 0.0°C , the melting point of solid water. The vapor pressure of the water was measured and found to be 4.58 torr. What is the vapor pressure of the ice in torr? Explain your answer.

Energy and The States of Matter (Section 6.15)

- 6.76** Using the specific heat data of Table 6.8, calculate the amount of heat (in calories) needed to increase the temperature of the following:
- 50 g of aluminum from 25°C to 55°C
 - 2500 g of ethylene glycol from 80°C to 85°C
 - 500 g of steam from 110°C to 120°C
- 6.77** Using the specific heat data of Table 6.8, calculate the amount of heat (in calories) needed to increase the temperatures of the following:
- 115 g of copper from 35°C to 75°C
 - 250 g of mercury from 110°C to 320°C
 - 5000 g of nitrogen from 200°C to 900°C
- 6.78** For solar energy to be effective, collected heat must be stored for use during periods of decreased sunshine. One proposal suggests that heat can be stored by melting solids that, upon solidification, would release the heat. Calculate the heat that could be stored by melting 1000 kg of each of the following solids. (NOTE: The water in each formula is included in the molecular weight.)
- Calcium chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$): melting point = 30.2°C , heat of fusion = 40.7 cal/g
 - Lithium nitrate ($\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$): melting point = 29.9°C , heat of fusion = 70.7 cal/g
 - Sodium sulfate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$): melting point = 32.4°C , heat of fusion = 57.1 cal/g
- 6.79** Why wouldn't a solid such as K_2SO_4 (melting point = 1069°C , heat of fusion = 50.3 cal/g) be suitable for use in a solar heat storage system? (See Exercise 6.78.)
- 6.80** Liquid Freon (CCl_2F_2) is used as a refrigerant. It is circulated inside the cooling coils of older refrigerators or freezers. As it vaporizes, it absorbs heat. How much heat can be removed by 2.00 kg of Freon as it vaporizes inside the coils of a refrigerator? The heat of vaporization of Freon is 38.6 cal/g.
- 6.81** Calculate the total amount of heat needed to change 500 g of ice at -10°C into 500 g of steam at 120°C . Do this by calculating the heat required for each of the following steps and adding to get the total:
- Step 1.** Ice (-10°C) \rightarrow ice (0°C)
 - Step 2.** Ice (0°C) \rightarrow water (0°C)
 - Step 3.** Water (0°C) \rightarrow water (100°C)
 - Step 4.** Water (100°C) \rightarrow steam (100°C)
 - Step 5.** Steam (100°C) \rightarrow steam (120°C)

Additional Exercises

- 6.82** What is the density of argon gas in g/mL at STP?
- 6.83** Explosives react very rapidly and produce large quantities of heat and gaseous products. When nitroglycerine explodes, several gases are produced:
- $$4\text{C}_3\text{H}_5\text{O}_9\text{N}_3(\ell) \rightarrow 12\text{CO}_2(\text{g}) + \text{O}_2(\text{g}) + 6\text{N}_2(\text{g}) + 10\text{H}_2\text{O}(\text{g})$$
- Suppose 10 g of nitroglycerine was sealed inside a 1.0-L soda bottle and detonated. Assume the bottle would not break, and the temperature immediately after detonation was 750 K. Calculate the pressure of the gases inside the bottle in atmospheres.
- 6.84** How many liters of oxygen gas, O_2 , will it take to completely react with 2.31 L of hydrogen gas, H_2 , to produce water? Assume both gases are at the same pressure and temperature. What type of reaction is this?
- 6.85** Review Table 6.4; then propose an explanation for the fact that hydrogen bonding decreases the vapor pressure of liquids made up of molecules with similar molecular weights.
- 6.86** Some people say they have a hard time breathing on top of a tall mountain because there is less oxygen in the air they breathe. Is this a true statement? Explain your answer.

Allied Health Exam Connection

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- 6.87** Definite shape and definite volume best describes a sample of:
- $\text{I}_2(\text{s})$
 - $\text{Br}_2(\text{l})$
 - $\text{Cl}(\text{g})$
 - $\text{F}_2(\text{g})$
- 6.88** Which of the following is NOT characteristic of gases?
- They have a definite volume and shape
 - They are low in density
 - They are highly compressible
 - They mix rapidly
- 6.89** Which of the following states has the highest average translational kinetic energy?
- solid
 - liquid
 - gas
 - none of the above
- 6.90** In which of the following states of matter are molecules most likely to move freely?
- solid
 - liquid
 - gas
 - all have similar freedom of movement
- 6.91** Which of the following indicates the relative randomness of molecules in the three states of matter?
- solid > liquid < gas
 - liquid < solid < gas
 - liquid > gas > solid
 - gas > liquid > solid
- 6.92** In the kinetic molecular theory of gases, which of the following statements concerning average speeds is true?
- Most of the molecules are moving at the average speed.
 - Any given molecule moves at the average speed most of the time.
 - When the temperature increases, more of the molecules will move at the new average speed.
 - When the temperature increases, fewer molecules will move at the new average speed.
- 6.93** All of the following statements underlie the kinetic molecular theory of gases EXCEPT:
- Gas molecules have no intermolecular forces.
 - Gas particles are in random motion.
 - Gas particles have no volume.
 - The average kinetic energy is proportional to the temperature ($^{\circ}\text{C}$) of the gas.
- 6.94** What are the differentiating factors between potential and kinetic energy?
- Properties—physical or chemical
 - State—solid or liquid
 - Temperature—high or low
 - Activity—in motion or in storage
- 6.95** The transformation of a solid directly into a gas is called:
- vaporization
 - ionization
 - sublimation
 - polarization
- 6.96** Evaporation can best be described as:
- the process in which molecules may have enough energy to leave the liquid phase and escape into the gaseous phase
 - a heating process
 - fusion
 - the process in which molecules in the solid phase absorb enough energy to begin the liquid phase

- 6.97** When a vapor condenses into a liquid:
- it absorbs heat
 - it generates heat
 - its temperature rises
 - its temperature drops
- 6.98** When solid iodine becomes gaseous iodine with no apparent liquid phase in between, the process is called:
- evaporation
 - condensation
 - sublimation
 - precipitation
- 6.99** What does the term *pressure* mean when applied to a gas?
- weight
 - how heavy the gas is
 - mass divided by volume
 - force exerted per unit area
- 6.100** When one liquid evaporates much faster than another liquid, the first liquid is said to be more:
- volatile
 - transient
 - viscous
 - evaporative
- 6.101** Which of the following laws is related to this expression:
 $P_T = P_1 + P_2 + P_3$?
- Boyle's law
 - Charles's law
 - Gay-Lussac's law
 - Dalton's law
- 6.102** Which law predicts that if the temperature (in Kelvin) doubles, the pressure will also double?
- Boyle's law
 - Charles's law
 - Gay-Lussac's law
 - Dalton's law
- 6.103** The inhaling and exhaling of air by the human lungs is mainly an application of:
- Boyle's law—the inverse relationship between the pressure and the volume of a gas.
 - The volume of a gas at standard temperature and pressure (STP).
 - Charles's law—the direct relationship between the temperature and the volume of a gas.
 - The number of O_2 and CO_2 particles per mole.
- 6.104** How much heat is required to raise the temperature of 100 grams of water from 25°C (near room temperature) to 100°C (its boiling point)? The specific heat of water is approximately 4.2 J per g-K.
- 3.2×10^4 J
 - 32 J
 - 4.2×10^4 J
 - 76 J
- 6.105** How many calories are required to change the temperature of 2,000 grams of H_2O from 20°C to 38°C ?
- 36 calories
 - 24 calories
 - 18 calories
 - 12 calories
- 6.106** If temperature and pressure are held constant for a sample of gas, and the number of moles is doubled, in what manner will the volume change?
- it will double
 - it will quadruple
 - it will be halved
 - there will be no change
- 6.107** A gas has a volume of 0.25 liter at a pressure of 1 atmosphere. If the volume increases to 0.50 liter and the temperature remains constant, the new pressure will be:
- 1 atmosphere
 - 0.5 atmosphere
 - 0.25 atmosphere
 - 2 atmospheres
- 6.108** Given 3.0 moles of krypton gas, $Kr(g)$, how many liters will this sample occupy at STP?
- 11.2
 - 22.4
 - 44.8
 - 67.2
- 6.109** A sample of helium at 25°C occupies a volume of 725 ml at 730 mm Hg. What volume will it occupy at 25°C and 760 mm Hg?
- 755 ml
 - 760 ml
 - 696 ml
 - 730 ml
- 6.110** One liter of a certain gas, under standard conditions, weighs 1.16 grams. A possible formula for the gas is:
- C_2H_2
 - CO
 - NH_3
 - O_2
- 6.111** A mixture consisting of 8.0 g of oxygen and 14 g of nitrogen is prepared in a container such that the total pressure is 750 mm Hg. The partial pressure of oxygen in the mixture is:
- 125 mm Hg
 - 500 mm Hg
 - 135 mm Hg
 - 250 mm Hg

- 6.112** A sample of nitrogen at 20°C in a volume of 875 ml has a pressure of 730 mm Hg. What will be its pressure at 20°C if the volume is changed to 955 ml?
- 750 mm Hg
 - 658 mm Hg
 - 797 mm Hg
 - 669 mm Hg
- 6.113** The weight in grams of 22.4 liters of nitrogen (atomic weight = 14) is:
- 3
 - 7
 - 14
 - 28
- 6.114** Water at sea level boils at what temperature?
- 100°F
 - 180°F
 - 212°C
 - 373°K
- 6.115** Which gas law states that the volume of a gas is inversely proportional to the pressure?
- Ideal gas law
 - Boyle's law
 - Combined gas law
 - Charles's law
- 6.116** When a liquid is at its boiling point, the vapor pressure of the liquid:
- is less than the external pressure on the liquid
 - is equal to the external pressure on the liquid
 - is greater than the external pressure on the liquid
 - can be either less or greater than the external pressure on the liquid

Chemistry for Thought

- 6.117** As solids are heated, they melt. Explain this in terms of the effect of temperature on cohesive and disruptive forces.
- 6.118** Explain how a hot-air balloon works in terms of gas densities.
- 6.119** Which of the following gases would you expect to behave most ideally: He, Ar, or HCl? Explain.
- 6.120** Refer to Figure 6.6 and do the calculation. When a gas is heated, it expands. Explain how the gas in a hot-air balloon remains at constant pressure as the gas is heated. Hot-air balloons do *not* stretch.
- 6.121** Refer to Figure 6.7 and answer the question. Would a basketball that was inflated for use actually contain the number of moles you calculated? Explain.
- 6.122** Refer to Figure 6.9 and answer the question. Calculate the actual time factor for the relative rate of deflation for the two gases, that is, twice as fast and so on.
- 6.123** Refer to Figure 6.12 and answer the question. Water is sometimes made safe to drink by boiling. Explain why this might not work if you attempted to do it in an open pan on the summit of Mount Everest.
- 6.124** Refer to Figure 6.15 and answer the question. Suppose a sample of water was heated to the boiling point in a glass beaker, using a single burner. What would happen to the temperature of the boiling water if a second burner was added to help with the heating? Explain.
- 6.125** Suppose you put four 250-mL bottles of water into an ice chest filled with crushed ice. If the bottles were initially at a temperature of 23°C, calculate the number of grams of ice that would have to melt in order to cool the water in the bottles to 5°C. Assume the density of water is 1.00g/mL.

Solutions and Colloids


7



Learning Objectives


When you have completed your study of this chapter, you should be able to:

- 1 Classify mixtures as solutions or non-solutions based on their appearance. (Section 7.1)
- 2 Demonstrate your understanding of terms related to the solubility of solutes in solution. (Section 7.2)
- 3 Predict in a general way the solubilities of solutes in solvents on the basis of molecular polarity. (Section 7.3)
- 4 Calculate solution concentrations in units of molarity, weight/weight percent, weight/volume percent, and volume/volume percent. (Section 7.4)
- 5 Describe how to prepare solutions of specific concentration using pure solutes and solvent, or solutions of greater concentration than the one desired. (Section 7.5)
- 6 Do stoichiometric calculations based on solution concentrations. (Section 7.6)
- 7 Do calculations based on the colligative solution properties of boiling point, freezing point, and osmotic pressure. (Section 7.7)
- 8 Describe the characteristics of colloids. (Section 7.8)
- 9 Describe the process of dialysis, and compare it to the process of osmosis. (Section 7.9)



Urine, a solution formed in the kidneys, is an excellent indicator of the body's state of health. Urinalysis is an essential part of a physical examination or a diagnosis of disease. Here, a **clinical laboratory technician** examines a urine sample before preparing it for testing. In this chapter you will learn many of the important characteristics of solutions.

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 Online homework for this chapter may be assigned in OWL.

Earlier, homogeneous matter was classified into two categories—pure substances and mixtures (see Figure 1.5). Since then, the discussion has been limited to pure substances. We now look at homogeneous mixtures called solutions and their distant relatives, colloidal suspensions.

Solutions and colloidal suspensions are very important in our world. They bring nutrients to the cells of our bodies and carry away waste products. The ocean is a solution of water, sodium chloride, and many other substances (even gold). Many chemical reactions take place in solution—including most of those discussed in this book.

7.1 Physical States of Solutions

Learning Objective

1. Classify mixtures as solutions or nonsolutions based on their appearance.

Solutions are homogeneous mixtures of two or more substances in which the components are present as atoms, molecules, or ions. These uniformly distributed particles are too small to reflect light, and as a result solutions are transparent (clear); light passes through them. In addition, some solutions are colored. The component particles are in constant motion (remember the kinetic theory, Section 6.2) and do not settle under the influence of gravity.

In most solutions, a larger amount of one substance is present compared to the other components. This most abundant substance in a solution is called the **solvent**, and any other components are called **solutes**. Most people normally think of solutions as liquids, but solutions in solid and gaseous forms are known as well. The state of a solution is often the same as the state of the solvent. This is illustrated by Table 7.1, which lists examples of solutions in various states. The original states of the solvents and solutes are given in parentheses. Solution formation takes place when one or more solutes **dissolve** in a solvent.

Example 7.1

Identify the solvent and solute(s) in each of the following solutions:

- a. A sample of natural gas contains 97% methane (CH_4), 1.5% ethane (C_2H_6), 1% carbon dioxide (CO_2), and 0.5% nitrogen (N_2).
- b. The label on a bottle of Scotch whiskey says, among other things, 86 proof. This means the contents contain 43% ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$). Assume water to be the only other component.
- c. The physiological saline solution used in hospitals contains 0.9 g NaCl for each 100 g water.

Solution

- a. Methane is present in the largest amount; it is the solvent. All other components are solutes.
- b. The whiskey is 43% alcohol and 57% water. Thus, water is the solvent and alcohol the solute. The whiskey actually contains small amounts of many other components, which impart flavor and color. These components are also solutes.
- c. Water is the component present in the larger amount and is therefore the solvent.

Learning Check 7.1

Identify the solvent and solute(s) in the following solutions:

- a. White gold is a solid solution containing 58.3% gold, 17.0% copper, 7.7% zinc, and 17.0% nickel.
- b. Clean, dry air contains about 78.1% nitrogen, 21.0% oxygen, 0.9% argon, and very small amounts of other gases.

solution A homogeneous mixture of two or more substances in which the components are present as atoms, molecules, or ions.

solvent The substance present in a solution in the largest amount.

solute One or more substances present in a solution in amounts less than that of the solvent.

dissolving A term used to describe the process of solution formation when one or more solutes are dispersed in a solvent to form a homogeneous mixture.

Table 7.1 Solutions in Various States

Solution	Solution State	Solvent	Solute
Salt water	Liquid	Water (liquid)	Sodium chloride (solid)
Alcoholic beverage	Liquid	Water (liquid)	Alcohol (liquid)
Carbonated water	Liquid	Water (liquid)	Carbon dioxide (gas)
Gold alloy (jewelry)	Solid	Gold (solid)	Copper (solid)
Gold amalgam	Solid	Gold (solid)	Mercury (liquid)
Hydrogen in palladium	Solid	Palladium (solid)	Hydrogen (gas)
Air	Gaseous	Nitrogen (gas)	Oxygen (gas)
Humid oxygen	Gaseous	Oxygen (gas)	Water (liquid)
Camphor in nitrogen	Gaseous	Nitrogen (gas)	Camphor (solid)

7.2 Solubility

Learning Objective

- Demonstrate your understanding of terms related to the solubility of solutes in solution.

A few experiments with water, sugar, cooking oil, and rubbing alcohol (isopropyl alcohol) illustrate some important concepts associated with solution formation. Imagine you have three drinking glasses, each containing 100 mL (100 g) of pure water. You begin by adding small amounts of the other three substances to the glasses. The mixtures are stirred well, with results shown in ▶ Figure 7.1A. The sugar and alcohol form homogeneous mixtures (solutions) with the water, while the oil forms a two-layer (heterogeneous) mixture. **Soluble substances** such as the sugar and alcohol dissolve completely in the solvent and form solutions. **Insoluble substances** do not dissolve in the solvent. The term **immiscible** is used to describe a liquid solute that does not dissolve in a liquid solvent.

The experiments are continued by adding more sugar, alcohol, and oil to the water samples. This ultimately leads to the situation shown in Figure 7.1B. Regardless of the amount of alcohol added, a solution forms. In fact, other experiments could be done that show that water and isopropyl alcohol are completely soluble in each other and will mix in any proportion. Sugar behaves differently. About 204 g can be dissolved in the 100 mL of water (at 20°C), but any additional sugar simply sinks to the bottom of the glass and remains undissolved. Thus, the sugar has a solubility in water of 204 g/100 g H₂O. The term **solubility** refers to the maximum amount of solute that can dissolve in a specific amount of solvent at a specific temperature. With the oil–water mixture, any additional oil simply floats on the surface of the water along with the oil added initially.

The solubilities of a number of solutes in water are given in ▶ Table 7.2. The use of specific units, such as grams of solute per 100 g of water, makes it possible to compare solubilities precisely. However, such precision is often unnecessary, and when this is the case, the approximate terms defined in ▶ Table 7.3 will be used.

A solution in which the maximum amount of solute has been dissolved in a quantity of solvent is called a **saturated solution**. The final sugar solution described in the earlier experiments (204 g in 100 g H₂O) was a saturated solution. Solutions in which the amount of solute dissolved is greater than the solute solubility are called **supersaturated solutions**. Supersaturated solutions are usually prepared by forming a nearly saturated solution at a high temperature and then cooling the solution to a lower temperature at which the solubility is lower. Such solutions are not stable. The addition of a small amount of solid solute (or even a dust particle) will usually cause the excess solute to crystallize out

soluble substance A substance that dissolves to a significant extent in a solvent.

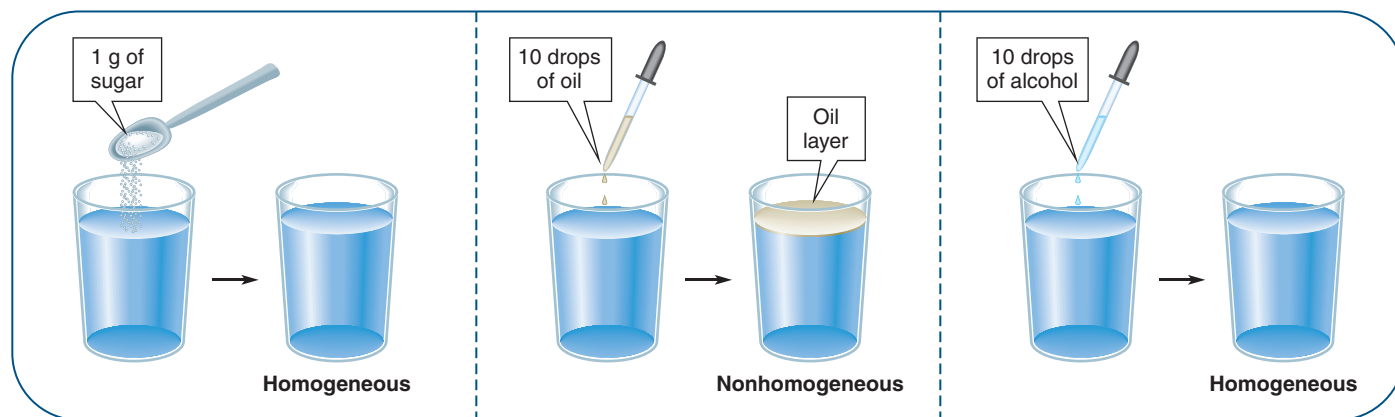
insoluble substance A substance that does not dissolve to a significant extent in a solvent.

immiscible A term used to describe liquids that are insoluble in each other.

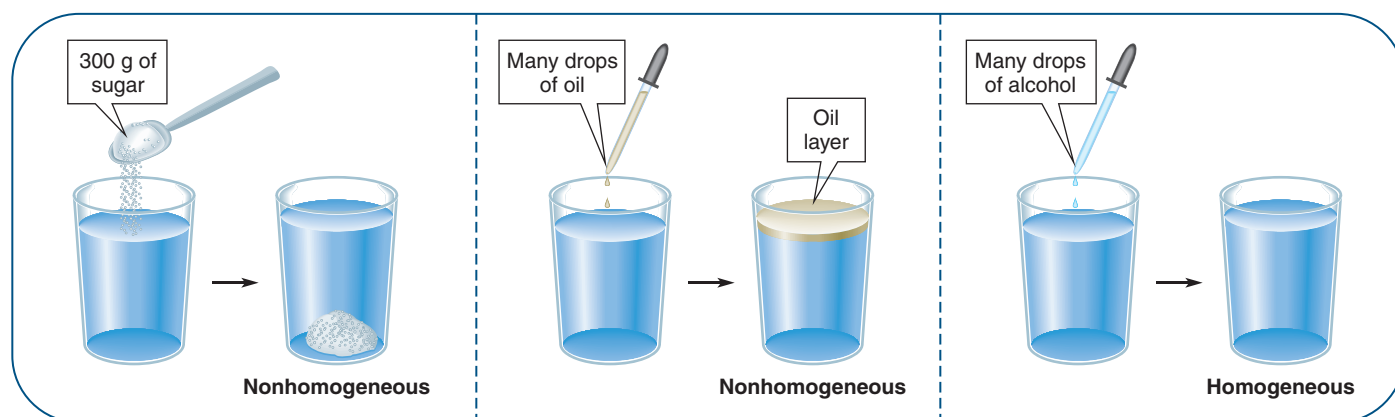
solubility The maximum amount of solute that can be dissolved in a specific amount of solvent under specific conditions of temperature and pressure.

saturated solution A solution that contains the maximum amount possible of dissolved solute in a stable situation under the prevailing conditions of temperature and pressure.

supersaturated solution An unstable solution that contains an amount of solute greater than the solute solubility under the prevailing conditions of temperature and pressure.



A Small amounts of substance added



B Larger amounts of substance added

Figure 7.1 The homogeneity of solutions and mixtures of sugar (limited solubility), cooking oil (immiscible), and alcohol (completely soluble).

of solution until the solution becomes saturated (see ► Figure 7.2). The temperature dependence of solute solubility is illustrated in ► Figure 7.3.

Whereas the solubility of most liquids and solids in water increases with temperature, the solubility of most gases in water decreases as the temperature increases (see the SO_2 curve in Figure 7.3). This is easily demonstrated for gaseous CO_2 by opening both a cold and a warm carbonated beverage. The solubility of gaseous solutes is also influenced significantly by pressure; the effect on liquid or solid solutes is minimal. It has been found that the solubility of many gases is directly proportional to the pressure of the gas above the solution at constant temperature. Thus, if the gas pressure is doubled, the solubility doubles.

The pressure dependence of gas solubility provides the “sparkle” for carbonated beverages. The cold beverage is saturated with CO_2 and capped under pressure. When the bottle is opened, the pressure is relieved, and the gas, now less soluble, comes out of solution as fine bubbles. A similar effect sometimes takes place in the bloodstream of deep-sea divers. While submerged, they inhale air under pressure that causes nitrogen to be more soluble in the blood than it is under normal atmospheric pressure. If the diver is brought to the lower pressure on the surface too quickly, the excess dissolved nitrogen comes out of solution and forms bubbles in the blood and joints. The result, called decompression sickness or the bends, is painful and dangerous. The chances of getting the bends are decreased by breathing a mixture of oxygen and helium rather than air (oxygen and nitrogen) because helium is less soluble in the body fluids than nitrogen.

Table 7.2 Examples of Solute Solubilities in Water (0°C)

Solute		Solubility (g solute/100 g H ₂ O)
Name	Formula	
Ammonium chloride	NH ₄ Cl	29.7
Ammonium nitrate	NH ₄ NO ₃	118.3
Ammonium orthophosphate	NH ₄ H ₂ PO ₄	22.7
Ammonium sulfate	(NH ₄) ₂ SO ₄	70.6
Calcium carbonate	CaCO ₃	0.0012
Calcium chloride	CaCl ₂	53.3
Calcium sulfate	CaSO ₄	0.23
Potassium carbonate	K ₂ CO ₃	101
Potassium chloride	KCl	29.2
Sodium bicarbonate	NaHCO ₃	6.9
Sodium bromide	NaBr	111
Sodium carbonate	Na ₂ CO ₃	7.1
Sodium chloride	NaCl	35.7
Sodium iodide	NaI	144.6
Ascorbic acid (vitamin C)	C ₆ H ₈ O ₆	33
Ethyl alcohol	C ₂ H ₅ OH	∞ ^a
Ethylene glycol (antifreeze)	C ₂ H ₄ (OH) ₂	∞
Glycerin	C ₃ H ₅ (OH) ₃	∞
Sucrose (table sugar)	C ₁₂ H ₂₂ O ₁₁	179.2

^aSoluble in all proportions.

Table 7.3 Approximate Solubility Terms

Solute Solubility (g solute/100 g H ₂ O)	Solubility Term
Less than 0.1	Insoluble
0.1–1	Slightly soluble
1–10	Soluble
Greater than 10	Very soluble



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1

A supersaturated solution.



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2

Seed crystal is added and induces rapid crystallization.



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3

After the excess solute is crystallized, the remaining solution is saturated.

Figure 7.2 Crystallization converts a supersaturated solution to a saturated solution.

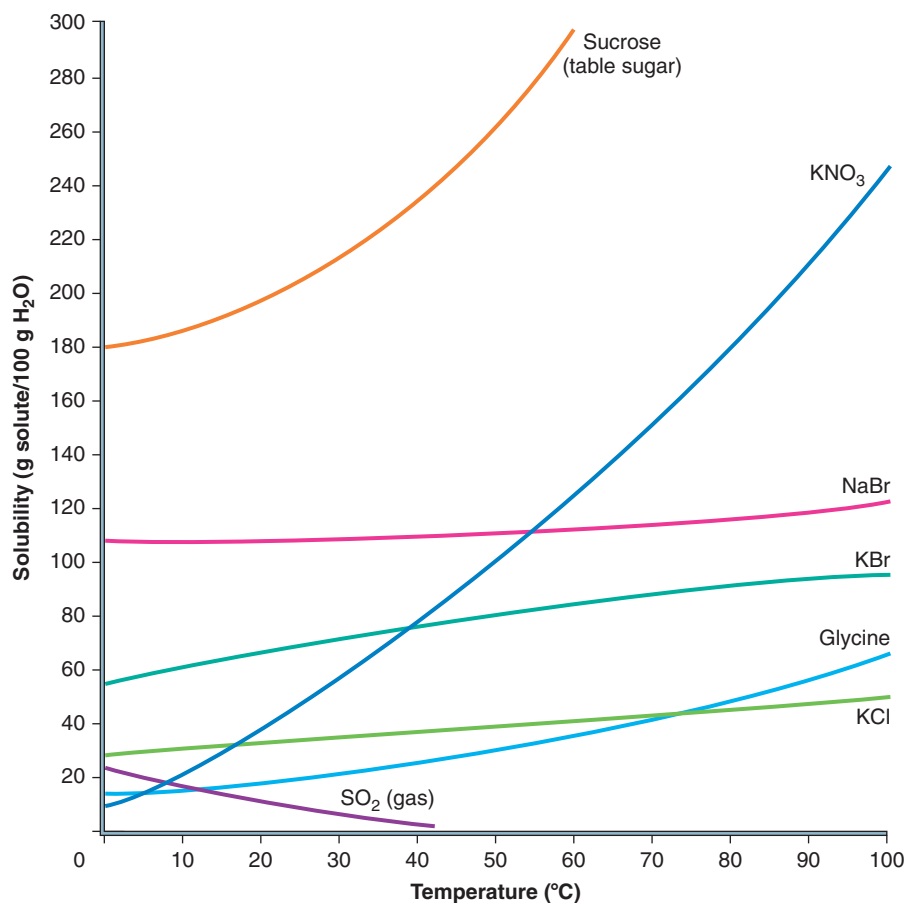


Figure 7.3 The effect of temperature on solute solubility.

Example 7.2

A 260-g sample of table sugar is added to 100 g of water at 70°C. The sugar dissolves completely. The resulting solution is allowed to cool slowly. At 30°C, crystals of sugar begin to form and increase in size as the solution cools to 20°C. Refer to Figure 7.3 and describe the nature of the solution at 70°, 60°, 50°, 40°, 30°, and 20°C.

Solution

The solubility of sugar is greater than 260 g/100 g H₂O at all temperatures above 50°C. Therefore, the solution is unsaturated at 70°C and 60°C. At 50°C, the solubility is equal to the amount dissolved, so the solution is saturated. At 40°C, the solution contains more dissolved sugar than it should on the basis of solubility, and the solution is supersaturated. At 30°C, the excess sugar crystallizes from solution, and the resulting solution becomes saturated. From that point, excess sugar continues to crystallize from the solution, and the solution remains saturated to 20°C.

Learning Check 7.2 Refer to Figure 7.3. Saturated solutions of potassium nitrate (KNO₃) and sodium bromide (NaBr) are made at 80°C. Which solution contains more solute per 100 g of H₂O? The solutions are cooled to 50°C, and excess solute crystallizes out of each solution. Which solution at 50°C contains more solute per 100 g of H₂O? Are the solutions saturated at 50°C?

7.3 The Solution Process

Learning Objective

3. Predict in a general way the solubilities of solutes in solvents on the basis of molecular polarity.

The how and why of solution formation are the topics of this section. How are solute particles removed from the bulk solute and uniformly distributed throughout the solvent? Why are some solutes very soluble whereas others are not?

Consider the formation of a saltwater solution. Earlier we pointed out (Section 4.2) that solid ionic compounds are collections of ions held together by attractions between the opposite ionic charges. When an ionic compound dissolves, the orderly ionic arrangement is destroyed as the interionic attractions are overcome. Thus, the attractive forces between water molecules and ions must be stronger than the interionic attractions within the crystal.

The solution-forming process for an ionic solute is represented in Figure 7.4. When the solid ionic crystal is placed in water, the polar water molecules become oriented so that the negative oxygen portion points toward positive sodium ions, and the positive hydrogen portion points toward negative chloride ions. As the polar water molecules begin to surround ions on the crystal surface, they tend to create a shielding effect that reduces the attraction between the ion and the remainder of the crystal. As a result, the ion breaks away from the crystal surface and is surrounded by water molecules. Ions surrounded by water molecules in solution are called **hydrated ions**. As each ion leaves the surface, others are exposed to the water, and the crystal is picked apart ion by ion. Once in solution, the hydrated ions are uniformly distributed by stirring or by random collisions with other molecules or ions.

The random motion of solute ions in solution causes them to collide with one another, with solvent molecules, and occasionally with the surface of any undissolved solute. Ions undergoing such collisions occasionally stick to the solid surface and thus leave the solution. When the number of ions in solution is low, the chances for collision with the undissolved solute are low. However, as the number of ions in solution increases, so do the chances for such collisions, and more ions leave the solution and become attached once again to the solid. Eventually, the number of ions in solution reaches a level at which ions return to the undissolved solute at the same rate as other ions leave. At this point the solution is saturated, an equilibrium condition. Even though the processes of leaving and

hydrated ion An ion in solution that is surrounded by water molecules.

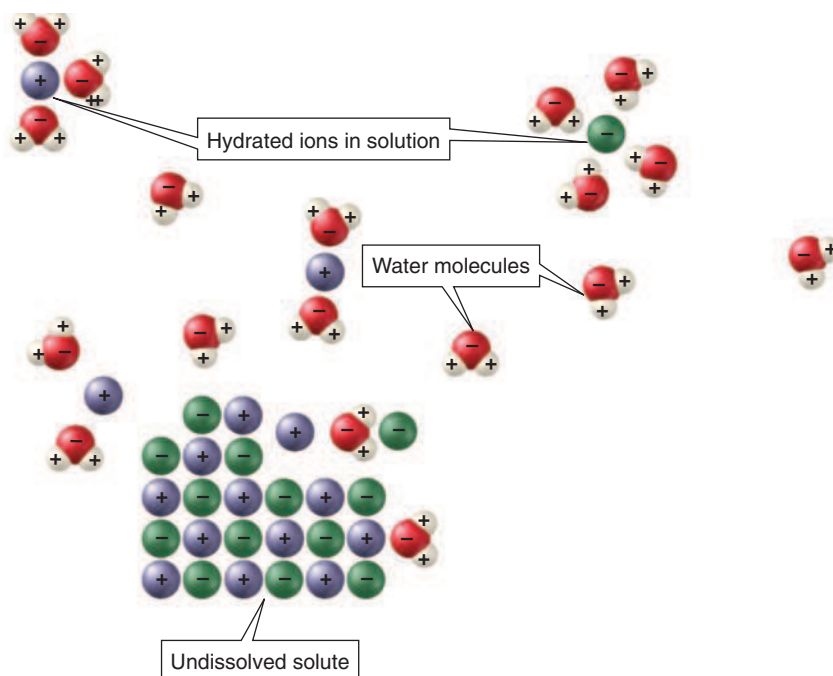


Figure 7.4 The dissolving of an ionic substance in water.

returning continue, no net changes in the number of ions in solution or the amount of undissolved solute can be detected as time passes, and an experimenter would observe that no more solid solute dissolves.

Supersaturated solutions form when there are no sites with which the excess solute particles can collide. The addition of such sites in the form of a seed crystal of solute causes the excess solute to crystallize from solution very quickly.

Polar but nonionic solutes such as sugar dissolve in water in much the same way as ionic solutes. The only difference is the attraction of polar water molecules to both poles of the solute molecules. The process is represented in [Figure 7.5](#).

This solution-forming process also explains the low solubility of some solutes. A solute will not dissolve in a solvent if (1) the forces between solute particles are too strong to be overcome by interactions with solvent particles or (2) the solvent particles are more strongly attracted to each other than to solute particles.

The cooking oil of the earlier experiment did not dissolve in water because the polar water molecules were attracted to each other more strongly than they were to the nonpolar oil molecules. The cooking oil will dissolve in a nonpolar solvent such as gasoline or carbon tetrachloride (CCl_4). In these solvents, the weak forces between oil molecules and solvent molecules are no stronger than the weak forces between nonpolar solvent molecules. A good rule of thumb is “like dissolves like.” Thus, polar solvents will dissolve polar or ionic solutes, and nonpolar solvents will dissolve nonpolar or nonionic solutes.

These generalizations apply best to nonionic compounds. Some ionic compounds (such as CaCO_3 and CaSO_4) have very low solubilities in water (see Table 7.2). Both the attractive forces between ions and the attraction of polar solvent molecules for ions are electrical and depend on such characteristics as ionic charge and size. Changes in ionic compounds that increase the attractive forces between ions also increase the forces between ions and polar solvent molecules, but not always by the same amount. Thus, simple rules for quantitatively predicting the water solubility of ionic compounds are not available. (We can’t easily predict how many grams will dissolve in a specific quantity of water.) However, ionic compounds are generally insoluble in nonpolar solvents; they usually follow the solubility guidelines given in [Table 7.4](#) when water is the solvent.

Figure 7.5 The dissolving of a polar solute in water.

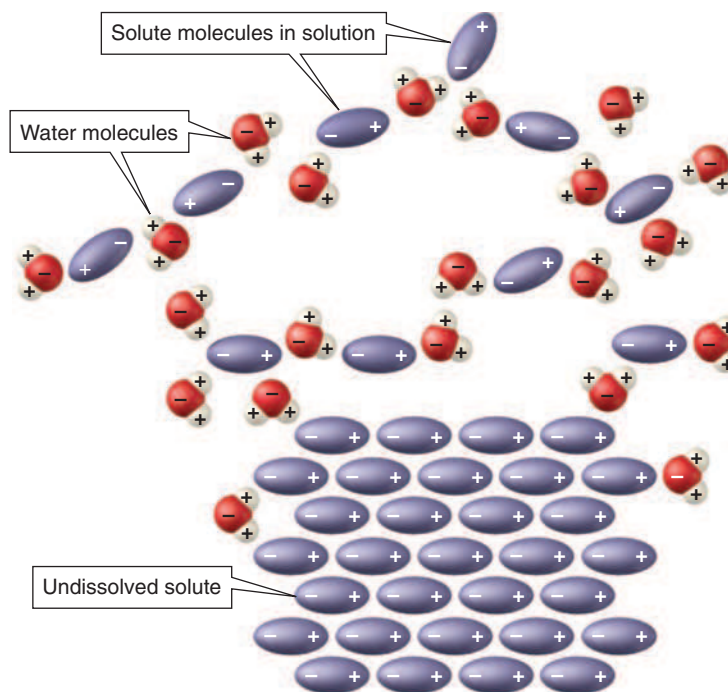


Table 7.4 General Solubilities of Ionic Compounds in Water

Compounds	Solubility	Exceptions
Group IA (Na^+ , K^+ , etc.) and NH_4^+	Soluble	
Nitrates (NO_3^-)	Soluble	
Acetates ($\text{C}_2\text{H}_3\text{O}_2^-$)	Soluble	
Chlorides (Cl^-)	Soluble	Chlorides of Ag^+ , Pb^{2+} , Hg^+ (Hg_2^{2+})
Sulfates (SO_4^{2-})	Soluble	Sulfates of Ba^{2+} , Sr^{2+} , Pb^{2+} , Hg^+ (Hg_2^{2+})
Carbonates (CO_3^{2-})	Insoluble ^a	Carbonates of group IA and NH_4^+
Phosphates (PO_4^{3-})	Insoluble ^a	Phosphates of group IA and NH_4^+

^aMany hydrogen carbonates (HCO_3^-) and phosphates (HPO_4^{2-} , H_2PO_4^-) are soluble.

Example 7.3

Predict the solubility of the following solutes in the solvent indicated:

- ammonia gas (NH_3) in water
- oxygen gas (O_2) in water
- $\text{Ca}(\text{NO}_3)_2$ in water
- $\text{Mg}_3(\text{PO}_4)_2$ in water
- paraffin wax (nonpolar) in CCl_4

Solution

- Soluble: NH_3 is polar—like dissolves like. The actual solubility at 20°C is 51.8 g/100 g H_2O .
- Insoluble: O_2 is nonpolar. The actual solubility at 20°C is 4.3×10^{-3} g/100 g H_2O .
- Soluble: nitrates are soluble in water (Table 7.4).
- Insoluble: phosphates are insoluble except those of group IA(1) and NH_4^+ (Table 7.4).
- Soluble: CCl_4 is nonpolar—like dissolves like.

Learning Check 7.3

- Refer to Table 7.4 and decide which of the following salts you would use as a solute if you wanted to prepare a solution that contained as many barium ions (Ba^{2+}) as possible: BaSO_4 , $\text{Ba}(\text{NO}_3)_2$, or BaCO_3 . Explain your answer.
- A common sight on the evening TV news since the late 1960s is sea birds soaked with crude oil being cleaned by concerned people. Which of the following do you think is used to clean the oil from the birds? Explain your answer. Light mineral oil, purified water, seawater, or gasoline.

Be careful not to confuse solute solubility with the rate at which a solute dissolves. Under some conditions, even a very soluble solute will dissolve slowly—for example, a lump of rock candy (sugar) dissolves much more slowly than an equal weight of granulated sugar. The dissolving rate can be increased in a number of ways (see Figure 7.6):

- Crushing or grinding the solute—small particles provide more surface area for solvent attack and dissolve more rapidly than larger particles.
- Heating the solvent—solvent molecules move faster and have more frequent collisions with solute at higher temperatures.
- Stirring or agitating the solution—stirring removes locally saturated solution from the vicinity of the solute and allows unsaturated solvent to take its place.



Figure 7.6 Heat and agitation increase the rate at which solutes dissolve. Will sugar dissolve faster in hot tea or iced tea?

Oral Rehydration Therapy



Dehydration, the excessive loss of water from the body, can result from a number of causes, including severe episodes of diarrhea or vomiting, and excessive sweating without proper fluid intake. The condition can be life threatening when it is severe enough and goes untreated. Dehydration is serious because the body loses electrolytes such as sodium, potassium, and chloride ions along with water. When the electrolyte balance in the body is upset, many organs, including the heart, cannot function properly. Small children are especially susceptible to dehydration caused by diarrhea because their small bodies do not have much of a fluid reserve, and it doesn't take much fluid loss to get their electrolytes out of balance.

Oral rehydration therapy (ORT) is a simple and effective way to treat or prevent dehydration and the accompanying electrolyte loss, especially if the dehydration is caused by diarrhea. Oral rehydration therapy was developed in the 1950s for use in developing countries where diarrhea-producing diseases like cholera, combined with unsanitary water and food, cause the death of an estimated 4 million children annually. The threat to children in developed countries is not nearly as great; an estimated 500 children die annually from diarrhea in the United States.

The materials used for ORT are simple mixtures of water, salts, and carbohydrates. These materials are regulated by the FDA as a medical food, and are available in most grocery and drug stores. A list of ingredients from the label of the liquid form of a popular ORT product includes water; the two carbohydrate sugars dextrose and fructose; citric acid; and the salts potassium citrate, sodium citrate, and sodium chloride. This material is available in an unflavored form, and in several flavors, such as berry and bubblegum, to appeal to children. The product also comes in the form of a powder that has to be dissolved in water before use. A third form consists of liquid sealed in plastic sleeves that can be frozen and then eaten like popular frozen treats.

The appropriate dosage for ORT products depends on the weight of the child; the directions included on the product labels should be read and followed. Many pediatricians suggest that parents of young children should include at least one bottle of oral rehydration fluid in the family medicine chest. The low cost of the commercially available materials makes it possible for most families to follow this prudent advice.

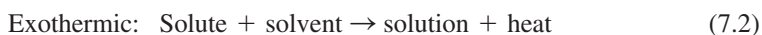
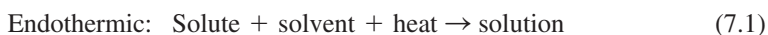


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Oral rehydration therapy products are available in numerous forms and flavors.

Heat is usually absorbed or released when a solute dissolves in a solvent. When heat is absorbed, the process is endothermic, and the solution becomes cooler. The fact that heat absorption leads to cooling might sound strange, and it needs to be explained. The heat is absorbed by the interacting solvent and solute molecules, and it is removed from the solvent molecules that are not involved in the actual attack on the solute. Since most of the solvent is in the latter category, the entire solution becomes cooled.

When heat is released, the process is exothermic, and the solution temperature increases, this time because the heat released by the interacting molecules is absorbed by the uninvolved solvent. This behavior is the more common one. These processes can be represented by equations:



An endothermic solution process is the basis for commercially available instant cold packs. Water is sealed in a thin plastic bag and placed inside a larger, stronger bag together with a quantity of solid solute (NH_4Cl or NH_4NO_3). When the inner bag is broken by squeezing, the solid dissolves in the water, heat is absorbed, and the mixture becomes quite cold (see [Figure 7.7](#)).



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- 1c Solid NaOH not yet added to water.



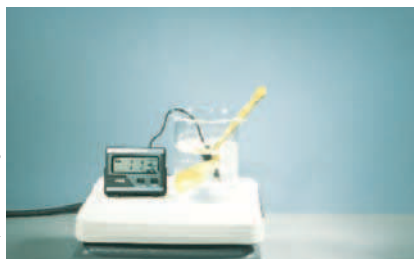
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- 2c Solution becomes hot when NaOH dissolves in water.



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- 1c Solid NH_4NO_3 not yet added to water.



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- 2c Solution becomes cool when NH_4NO_3 dissolves in water.

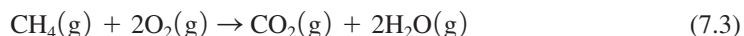
Figure 7.7 Exothermic (top) and endothermic (bottom) solution processes.

7.4 Solution Concentrations

Learning Objective

4. Calculate solution concentrations in units of molarity, weight/weight percent, weight/volume percent, and volume/volume percent.

In Chapter 5, quantitative calculations were done using equations for reactions such as the following:



The reaction represented by this equation, and most of the reactions we have discussed to this point in the book, involve pure substances as reactants and products. However, many of the reactions done in laboratories, and most of those that go on in our bodies, take place between substances dissolved in a solvent to form solutions. In our bodies, the solvent is almost always water. A double-replacement reaction of this type done in laboratories is represented by the following equation:



We remember from Chapter 5 that the coefficients in equations such as Equation 7.3 allow the relative number of moles of pure reactants and products involved in the reaction to be determined. These relationships coupled with the mole definition in terms of masses then yield factors that can be used to solve stoichiometric problems involving the reactants and products. Similar calculations can be done for reactions that take place between the solutes of solutions if the amount of solute contained in a specific quantity of the reacting solutions is known. Such relationships are known as solution **concentrations**. Solution concentrations may be expressed in a variety of units, but only two, molarity and percent-age, will be discussed at this time.

concentration The relationship between the amount of solute and the specific amount of solution in which it is contained.

molarity (M) A solution concentration expressed in terms of the number of moles of solute contained in a liter of solution.

The **molarity (M)** of a solution expresses the number of moles of solute contained in exactly 1 L of the solution:

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} \quad (7.5)$$

It is important to note that even though a concentration in molarity expresses the number of moles contained in 1 L of solution, the molarity of solutions that have total volumes different from 1 L can be calculated using Equation 7.5. We simply determine the number of moles of solute contained in a specified volume of solution, then express that volume in liters before substituting the values into Equation 7.5.

Example 7.4

Express the concentration of each of the following solutions in terms of molarity:

- a. 2.00 L of solution contains 1.50 mol of solute.
- b. 150 mL of solution contains 0.210 mol of solute.
- c. 315 mL of solution contains 10.3 g of isopropyl alcohol, $\text{C}_3\text{H}_7\text{OH}$.

Solution

- a. Because the data are given in terms of moles of solute and liters of solution, the data may be substituted directly into Equation 7.5:

$$M = \frac{1.50 \text{ mol solute}}{2.00 \text{ L solution}} = 0.750 \frac{\text{mol solute}}{\text{L solution}}$$

The solution is 0.750 molar, or 0.750 M.

- b. In this problem, the number of moles of solute is given, but the volume of solution is given in milliliters rather than liters. The volume must first be converted into liters, then the data may be substituted into Equation 7.5:

$$(150 \text{ mL solution}) \left(\frac{1 \text{ L}}{1000 \text{ mL}} \right) = 0.150 \text{ L solution}$$

$$M = \frac{0.210 \text{ mol solute}}{0.150 \text{ L solution}} = 1.40 \frac{\text{mol solute}}{\text{L solution}}$$

The solution is 1.40 molar, or 1.40 M.

- c. Before Equation 7.5 can be used, the number of moles of solute (isopropyl alcohol) must be determined. This is done as follows, where the factor

$$\frac{1 \text{ mol alcohol}}{60.1 \text{ g alcohol}}$$

comes from the calculated molecular weight of 60.1 u for isopropyl alcohol:

$$(10.3 \text{ g alcohol}) \left(\frac{1 \text{ mol alcohol}}{60.1 \text{ g alcohol}} \right) = 0.171 \text{ mol alcohol}$$

Next, this number of moles of solute and the solution volume expressed in liters are substituted into Equation 7.5:

$$M = \frac{0.171 \text{ mol alcohol}}{0.315 \text{ L solution}} = 0.543 \frac{\text{mol alcohol}}{\text{L solution}}$$

The solution is 0.543 molar, or 0.543 M.



Generally, the participation of youngsters in organized sports or other physical activities is considered to be desirable from a health point of view. Such behavior helps prevent the couch potato syndrome and obesity in children that have become health concerns in recent years. However, vigorous exercise in hot, humid weather can cause dehydration which can lead to mild or severe heat-related illnesses such as heat cramps, heat exhaustion or heat stroke.

Any child who exercises in hot weather may be at risk for dehydration. However, the concern is greatest for those participating in activities or organized sports such as football, soccer or cross-country running that take place during the hot days of late summer. Exercising children are particularly vulnerable to heat-related illnesses during hot weather if they:

1. Are just beginning to exercise after being relatively inactive for extended periods of time.
2. Are overweight or obese.
3. Have had a recent illness that caused vomiting or diarrhea.
4. Have had a previous heat-related illness.

Most heat-related illness occurs within the first few days of organized vigorous activity such as participation on a sports team. To avoid this, the activity should be relatively light during the first few days and should be increased gradually. During hot and humid conditions the American Academy of Pediatrics gives the following recommendations:

1. Sessions of intense activity should not last longer than 15 minutes with cooling off breaks between sessions.
2. Participants should drink plenty of fluids before the activities and during regularly scheduled breaks in the activities—even if the participants do not feel thirsty.
3. Where possible, the clothing of participants should consist of single layer of light-colored lightweight material.

Youthful participants as well as their parents, coaches or other supervisors should learn to identify the following early signs and

symptoms of dehydration: dry or sticky mouth, thirst, lethargy, irritability, headache, dizziness, cramps and excessive fatigue. Young participants should be taught the importance of recognizing these signs and symptoms in themselves, and the importance of reporting them to their parents, coach or supervisor. Embarrassment should not prevent the early detection and treatment of dehydration.



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Regular fluid intake is a must for participants in vigorous physical activities.

Learning Check 7.4 Express the concentrations of each of the following solutions in terms of molarity:

- a. 2.50 L of solution contains 1.25 mol of solute.
- b. 225 mL of solution contains 0.486 mol of solute.
- c. 100 mL of solution contains 2.60 g of NaCl solute.

Sometimes a detailed knowledge of the actual stoichiometry of a process involving solutions is not needed, but some information about the solution concentrations would be useful. When this is true, solution concentrations are often expressed as percentages. In general, a concentration in **percent** gives the number of parts of solute contained in 100 parts of solution. You saw in Section 1.10 that it is convenient to use a formula for percentage calculations because we seldom work with exactly 100 units of anything. The general formula used is:

$$\% = \frac{\text{part}}{\text{total}} \times 100$$

Three different percent concentrations for solutions are used. A **weight/weight percent** (abbreviated w/w) is the mass of solute contained in 100 mass units of solution. Thus, a

percent A solution concentration that expresses the amount of solute in 100 parts of solution.

weight/weight percent
A concentration that expresses the mass of solute contained in 100 mass units of solution.

12.0% (w/w) sugar solution contains 12.0 grams of sugar in each 100 g of solution. In terms of this concentration, the general formula for percent calculations becomes

$$\%(w/w) = \frac{\text{solute mass}}{\text{solution mass}} \times 100 \quad (7.6)$$

Any mass units may be used, but the mass of solute and solution must be expressed in the same units.

A more commonly used percent concentration is **weight/volume percent** (abbreviated w/v), which is the grams of solute contained in 100 mL of solution. In these units, a 12.0% (w/v) sugar solution would contain 12.0 g of sugar in each 100 mL of solution. This percent concentration is normally used when the solute is a solid and the solvent and resulting solutions are liquids. The general formula for the calculation of percent concentrations in these units is

$$\%(w/v) = \frac{\text{grams of solute}}{\text{milliliters of solution}} \times 100 \quad (7.7)$$

In weight/volume percent calculations, the solute amount is always given in grams, and the solution volume is always given in milliliters.

A percent concentration that is useful when the solute and solvent are either both liquids or both gases is **volume/volume percent** (abbreviated v/v). Concentrations given in these units express the number of volumes of solute found in 100 volumes of solution. For these units, the general percentage equation becomes

$$\%(v/v) = \frac{\text{solute volume}}{\text{solution volume}} \times 100 \quad (7.8)$$

Any volume units may be used, but they must be the same for both the solute and the solution.

Example 7.5

- A solution contains 100 g of water and 1.20 g of solute. What is the %(w/w) concentration?
- A solution is made by mixing 90.0 mL of alcohol with enough water to give 250 mL of solution. What is the %(v/v) concentration of alcohol in the solution?
- A 150-mL sample of saltwater is evaporated to dryness. A residue of salt weighing 27.9 g is left behind. Calculate the %(w/v) of the original saltwater.

Solution

- a. Equation 7.6 is used:

$$\%(w/w) = \frac{\text{solute mass}}{\text{solution mass}} \times 100 = \frac{1.20 \text{ g}}{101.2 \text{ g}} \times 100 = 1.19\% (w/w)$$

Note that the solution mass is the sum of the solvent (water) and solute masses.

- b. Equation 7.8 is used:

$$\%(v/v) = \frac{\text{solute volume}}{\text{solution volume}} \times 100 = \frac{90 \text{ mL}}{250 \text{ mL}} \times 100 = 36.0\% (v/v)$$

- c. Equation 7.7 is used after checking to make certain the amount of solute is given in grams and the solution volume is in mL:

$$\begin{aligned} \%(w/v) &= \frac{\text{grams of solute}}{\text{milliliters of solution}} \times 100 \\ &= \frac{27.9 \text{ g}}{150 \text{ mL}} \times 100 \\ &= 18.6\% (w/v) \end{aligned}$$

weight/volume percent A concentration that expresses the grams of solute contained in 100 mL of solution.

volume/volume percent A concentration that expresses the volume of solute contained in 100 volumes of solution.

Learning Check 7.5

- A solution is made by dissolving 0.900 g of salt in 100.0 mL of water. Assume that each milliliter of water weighs 1.00 g and that the final solution volume is 100.0 mL. Calculate the $\%(w/w)$ and $\%(w/v)$ for the solution using the assumptions as necessary.
- An alcoholic beverage is labeled 90 proof, which means the alcohol concentration is 45% (v/v). How many milliliters of pure alcohol would be present in 1 oz (30 mL) of the beverage?

7.5 Solution Preparation

Learning Objective

- Describe how to prepare solutions of specific concentration using pure solutes and solvent, or solutions of greater concentration than the one desired.

Solutions are usually prepared by mixing together proper amounts of solute and solvent or by diluting a concentrated solution with solvent to produce a solution of lower concentration. In the first method, the solute is measured out and placed in a container, and the correct amount of solvent is added. When the concentration is based on solution volume [$\%(v/v)$, $\%(w/v)$, and M], a volumetric flask or other container is used that, when filled to a specific mark, holds an accurately known volume (see Figure 7.8). When the concentration is based on solvent mass [$\%(w/w)$], the correct mass of solvent is added. This mass is usually converted to a volume by using the density, so that a volume of solvent can be measured rather than an amount weighed on a balance.

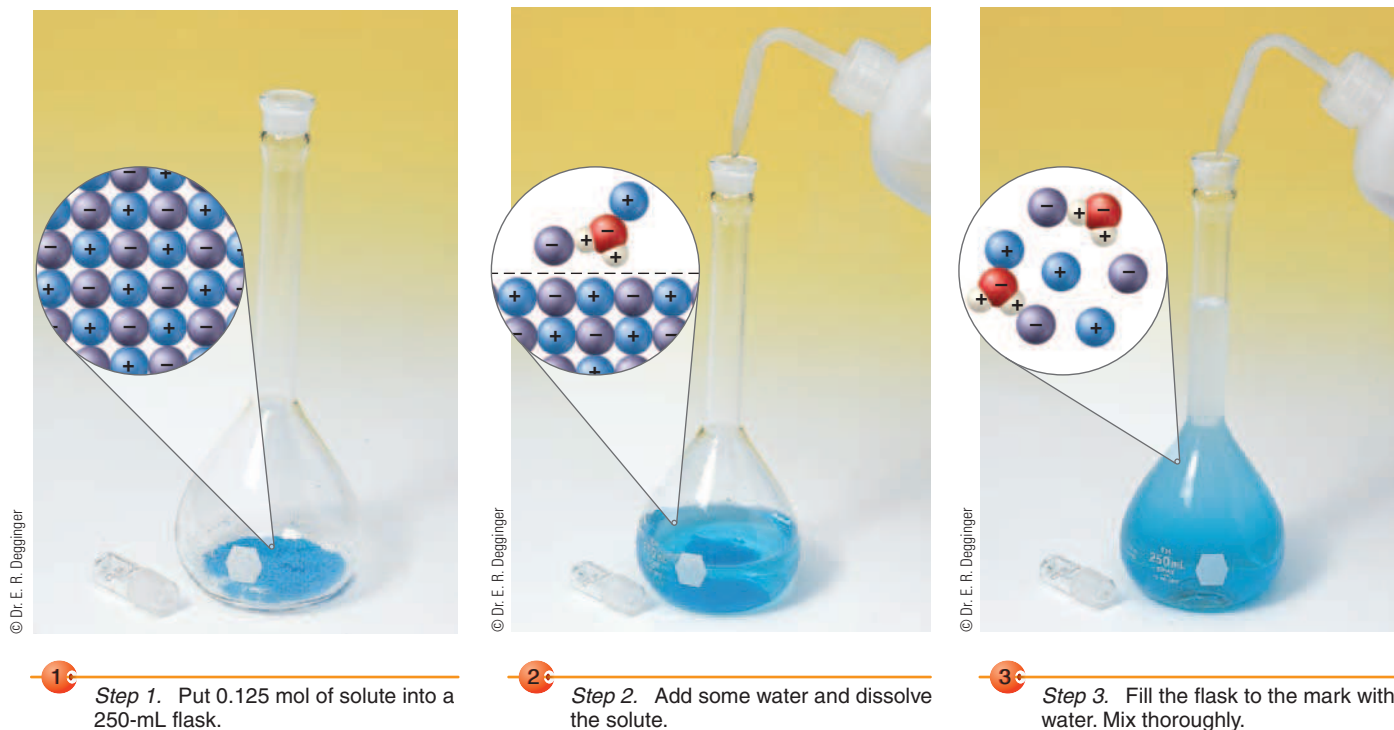


Figure 7.8 Preparation of a 0.500 M solution. Use the data given in the figure and show by a calculation that the resulting solution is 0.500 M.

Example 7.6

Describe how you would prepare the following solutions from pure solute and water:

- a. 1.00 L of 1.50 M CoCl_2 solution
- b. 250 mL of 0.900% (w/v) NaCl solution
- c. 500 mL of 8.00% (v/v) methyl alcohol solution

Solution

- a. According to Equation 7.5, molarity is the moles of solute per (divided by) the liters of solution containing the solute:

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

This equation can be rearranged to calculate the moles of solute required:

$$(M)(\text{liters of solution}) = \text{moles of solute}$$

By substituting the molarity and volume of the desired solution, the required number of moles of solute is determined:

$$\left(1.50 \frac{\text{mol}}{\text{L}}\right)(1.00 \text{ L}) = 1.50 \text{ mol}$$

The formula weight of CoCl_2 is 129.9 u. The mass of solute is calculated:

$$(1.50 \text{ mol CoCl}_2) \left(\frac{129.9 \text{ g CoCl}_2}{1 \text{ mol CoCl}_2} \right) = 195 \text{ g CoCl}_2$$

The solution is prepared by weighing out 195 g CoCl_2 , putting it into a 1-L volumetric flask, and adding enough water to fill the flask to the mark (see Figure 7.8). It is a good practice to let the solute dissolve completely in part of the solvent before filling the flask to the mark.

- b. Similarly, rearrange Equation 7.7, and use the result to calculate the amount of solute needed:

$$\%(\text{w/v}) = \frac{\text{grams of solute}}{\text{milliliters of solution}} \times 100$$

Therefore,

$$\frac{(\%)(\text{milliliters of solution})}{100} = \text{grams of solute}$$

Substitute percentage and solution volume:

$$\frac{(0.900\%)(250 \text{ mL})}{100} = 2.25 \text{ g NaCl}$$

Thus, the solution is prepared by putting 2.25 g NaCl into a 250-mL volumetric flask and adding water to the mark.

- c. Rearrange Equation 7.8, and use the result to calculate the volume of solute needed:

$$\%(\text{v/v}) = \frac{\text{solute volume}}{\text{solution volume}} \times 100$$

Therefore,

$$\frac{(\%)(\text{solution volume})}{100} = \text{solute volume}$$

Substitute percentage and solution volume:

$$\frac{(8.00\%)(500 \text{ mL})}{100} = 40.0 \text{ mL}$$

Thus, 40.0 mL methyl alcohol is put into a 500-mL volumetric flask, and water is added up to the mark.

► **Learning Check 7.6** Describe how you would prepare the following, using pure solute and water:

- 500 mL of 1.00 M MgCl_2 solution
- 100 mL of 12.0% (w/v) MgCl_2 solution
- 1.00 L of 20.0% (v/v) ethylene glycol solution

Solutions are often prepared by diluting a more concentrated solution with solvent (usually water) to produce a solution of lower concentration. Suppose, for example, that you want to prepare 250 mL of 0.100 M NaCl solution using a 2.00 M NaCl solution as the source of NaCl. First, calculate the number of moles of NaCl that would be contained in 250 mL of 0.100 M solution. Remember Equation 7.5,

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

which can be rearranged to

$$(M)(\text{liters of solution}) = \text{moles of solute}$$

So, the number of moles of NaCl contained in the desired solution is

$$\left(0.100 \frac{\text{mol}}{\text{L}}\right)(0.250 \text{ L}) = 0.0250 \text{ mol}$$

These moles of NaCl must be obtained from the 2.00 M NaCl solution. The volume of this solution that contains the desired number of moles can be obtained by rearranging Equation 7.5 a different way:

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

or

$$\text{liters of solution} = \frac{0.0250 \text{ mol}}{2.00 \text{ mol/L}} = 0.0125 \text{ L} = 12.5 \text{ mL}$$

Thus, the solution is prepared by putting 12.5 mL of 2.00 M NaCl solution into a 250-mL volumetric flask and adding water up to the mark. ► Figure 7.9 will help you understand this process.

The same result can be obtained by using a simplified calculation. Note that the product of concentration in molarity (M) and solution volume in liters will give the number of moles of solute in a sample of solution. In a dilution such as the one done above, the number of moles of solute taken from the concentrated solution and diluted with water is the same as the number of moles of solute in the resulting more dilute solution (see Figure 7.9). Thus, the following can be written:

$$M_c V_c = \begin{matrix} \text{solute moles in} \\ \text{concentrated solution} \end{matrix} = \begin{matrix} \text{solute moles in} \\ \text{dilute solution} \end{matrix} = M_d V_d$$

or

$$(C_c)(V_c) = (C_d)(V_d) \quad (7.9)$$

where the subscripts *c* and *d* refer to the more concentrated and dilute solutions, respectively, and *C* is used to represent any appropriate concentration. An advantage of using this equation is that any volume units may be used, as long as the same one is used for both



1 Step 1. 20.0 mL of 0.200 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution is withdrawn from a beaker using a pipette.

2 Step 2. The 20.0 mL of the 0.200 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution is put into a 100-mL flask.

3 Step 3. Water is added (while the solution is swirled) to fill the flask to the mark.

4 Step 4. The new solution is transferred to a bottle and labeled.

Figure 7.9 Preparation of a 0.0400 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution by dilution of a 0.200 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Use the data and show by a calculation that the new solution is 0.0400 M.

V_c and V_d . Also, Equation 7.9 is true for any solution concentration based on volume. This means that M, %(v/v), or %(w/v) concentrations can be used just as long as C_c and C_d are expressed in the same units.

Example 7.7

Use Equation 7.9 and describe how to prepare 250 mL of 0.100 M NaCl solution using a 2.00 M NaCl solution as the source of NaCl.

Solution

Equation 7.9 can be used to determine the volume of 2.00 M NaCl needed. The relationships between the terms in Equation 7.9 and the quantities of the problem are $C_c = 2.00$ M, $V_c =$ volume of 2.00 M NaCl needed, $C_d = 0.100$ M, and $V_d = 250$ mL. Substitution gives

$$(2.00 \text{ M})(V_c) = (0.100 \text{ M})(250 \text{ mL})$$

or

$$V_c = \frac{(0.100 \text{ M})(250 \text{ mL})}{(2.00 \text{ M})} = 12.5 \text{ mL}$$

Thus, we quickly find the volume of 2.00 M NaCl needs to be 12.5 mL, the same result found earlier. This volume of solution is put into a 250-mL flask, and water is added to the mark as before.

Learning Check 7.7 Use Equation 7.9 and describe how to prepare 500 mL of a 0.250 M NaOH solution from a 6.00 M NaOH solution.

7.6 Solution Stoichiometry

Learning Objective

- Do stoichiometric calculations based on solution concentrations.

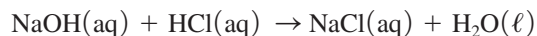
The stoichiometry calculations of solution reactions can be done using the factor-unit method. The sources of the needed factors will be the mole interpretation of the reactions

introduced as statement 2 in Section 5.9, and the molarities of the solutions involved in the reactions. Each known solution molarity will provide two factors. For example, the following two factors can be obtained based on a 0.400 M HCl solution:

$$\frac{0.400 \text{ mol HCl}}{1 \text{ L HCl soln.}} \quad \text{and} \quad \frac{1 \text{ L HCl soln.}}{0.400 \text{ mol HCl}}$$

Example 7.8

Solutions of NaOH and HCl react according to the following equation:



- What volume of a 0.250 M NaOH solution contains 0.110 moles of NaOH?
- What volume of a 0.200 M NaOH solution is needed to exactly react with 0.150 moles of HCl?
- What volume of a 0.185 M NaOH solution is needed to exactly react with 25.0 mL of 0.255 M HCl solution?

Solution

- The known quantity is 0.110 mol of NaOH, and the unit of the unknown quantity is a volume which we will express as L NaOH soln.

Step 1. 0.110 mol NaOH

Step 2. 0.110 mol NaOH = L NaOH soln.

Step 3. $0.110 \text{ mol NaOH} \times \frac{1 \text{ L NaOH soln.}}{0.250 \text{ mol NaOH}} = \text{L NaOH soln.}$

The factor $\frac{1 \text{ L NaOH soln.}}{0.250 \text{ mol NaOH}}$ came from the known molarity of the NaOH solution as described above.

Step 4. $0.110 \times \frac{1 \text{ L NaOH soln.}}{0.250} = 0.44 \text{ L NaOH soln.} = 0.440 \text{ L NaOH soln.}$

The calculator answer of 0.44 was rounded by adding a trailing zero so the answer had three significant figures to match the three significant figures in 0.110 and 0.250. The number 1 is an exact counting number.

- The known quantity is 0.150 mol HCl, and the unit of the unknown quantity is the volume of NaOH solution which we will express as L NaOH soln.

Step 1. 0.150 mol HCl

Step 2. 0.150 mol HCl = L NaOH soln.

Step 3. $0.150 \text{ mol HCl} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}} \times \frac{1 \text{ L NaOH soln.}}{0.200 \text{ mol NaOH}} = \text{L NaOH soln.}$

Note that two factors were needed to cancel the unit of the known quantity and generate the unit of the unknown quantity. The first factor came from statement 2 for the reaction:



Statement 2: $1 \text{ mol NaOH} + 1 \text{ mol HCl} \rightarrow 1 \text{ mol NaCl} + 1 \text{ mole H}_2\text{O}$

The second factor came from the 0.200 M concentration of the NaOH solution. Two factors were possible: $\frac{0.200 \text{ mol NaOH}}{1 \text{ L NaOH soln.}}$ and $\frac{1 \text{ L NaOH soln.}}{0.200 \text{ mol NaOH}}$. The second factor was used because it cancelled the *mol NaOH* unit and generated the *L NaOH soln.* unit.

$$\text{Step 4. } 0.150 \times \frac{1}{1} \times \frac{1 \text{ L NaOH soln.}}{0.200} = 0.75 \text{ L NaOH soln.} = 0.750 \text{ L NaOH soln.}$$

Once again, a zero was added to the calculator answer of 0.75 to give an answer with three significant figures to match the three in 0.150 and 0.200. Both of the 1 numbers are exact counting numbers.

- c. The known quantity is 25.0 mL of a 0.225 M HCl soln., and the unit of the unknown is the volume of a 0.185 M NaOH soln. which we will express as mL NaOH soln. to match the mL unit of the known quantity.

Step 1. 25.0 mL HCl soln.

Step 2. 25.0 mL HCl soln. = mL NaOH soln.

$$\begin{aligned} \text{Step 3. } 25.0 \text{ mL HCl soln.} \times \frac{0.225 \text{ mol HCl}}{1000 \text{ mL HCl soln.}} \\ \times \frac{1 \text{ mol NaOH}}{1 \text{ mol HCl}} \times \frac{1000 \text{ mL NaOH soln.}}{0.185 \text{ mol NaOH}} = \text{mL NaOH soln.} \end{aligned}$$

Note that three factors were needed. The first came from the molarity of the HCl solution with the solution volume expressed as 1000 mL rather than 1 L. The second factor came from statement 2 for the reaction as was done in part b. The third factor came from the molarity of the NaOH solution with the solution volume expressed as 1000 mL rather than 1 L.

$$\text{Step 4. } 25.0 \times \frac{0.225}{1000} \times \frac{1}{1} \times \frac{1000 \text{ mL NaOH soln.}}{0.185} = 30.4 \text{ mL NaOH soln.}$$

7.7 Solution Properties

Learning Objective

- Do calculations based on the colligative solution properties of boiling point, freezing point, and osmotic pressure.

The experiment represented in Figure 7.10 reveals an interesting property of some solutions. As shown by the figure, the circuit is completed and the light goes on only when the



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1

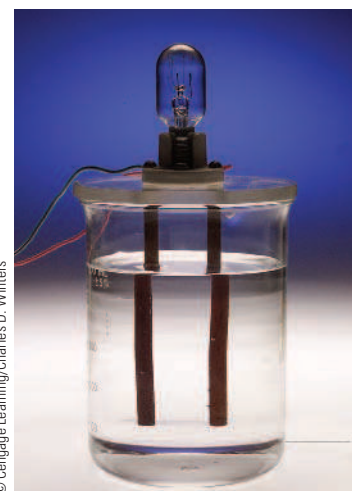
A solution of a strong electrolyte conducts electricity well.



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2

A solution of a weak electrolyte conducts electricity poorly.



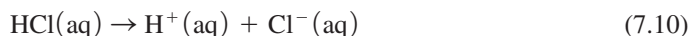
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3

A solution of a nonelectrolyte does not conduct electricity.

Figure 7.10 Electrical conductivity of solutions.

solution conducts electricity. Experiments of this type demonstrate that conductive solutions are formed when soluble ionic materials (Section 4.3), such as sodium chloride, or highly polar covalent materials (Section 4.9), such as hydrogen chloride, dissolve in water. Solutes that form conductive water solutions are called **electrolytes**, whereas solutes that form nonconductive solutions are called **nonelectrolytes**. Conductive solutions result when the dissolved solute dissociates, or breaks apart, to form ions, as shown in the following equations representing the dissociation into ions of polar covalent hydrogen chloride and ionic calcium nitrate:



Some electrolytes, such as HCl and $\text{Ca(NO}_3)_2$, dissociate essentially completely in solution and are called *strong electrolytes*. They form strongly conducting solutions. Other electrolytes, such as acetic acid (the acid found in vinegar), dissociate only slightly and form weakly conductive solutions. These solutes are classified as *weak electrolytes*. The solutes in nonconductive solutions dissolve in the solvent but remain in the form of uncharged molecules.

Besides electrical conductivity (or the lack of it), all solutions have properties that depend only on the concentration of solute particles present and not on the actual identity of the solute. Thus, these properties, called **colligative properties**, would be identical for water solutions containing 1 mol of sugar or 1 mol of alcohol per liter.

Three closely related colligative properties are vapor pressure, boiling point, and freezing point. Experiments demonstrate that the vapor pressure of water (solvent) above a solution is lower than the vapor pressure of pure water (see Figure 7.11). This behavior causes the boiling point of solutions to be higher than the boiling point of the pure solvent used in the solutions, and the freezing point to be lower (see Table 7.5).

The boiling and freezing point differences between pure solvent and solutions can be calculated by using an equation of the general form

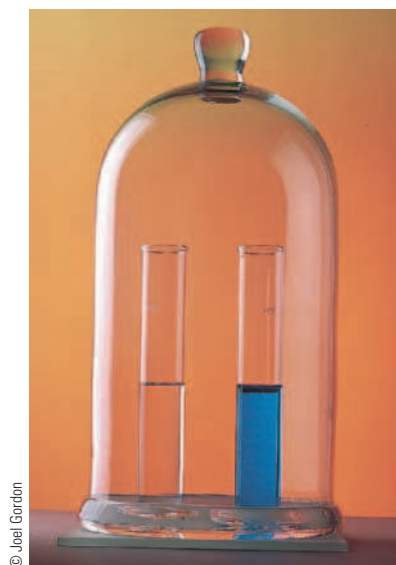
$$\Delta t = nkm \quad (7.12)$$

In this equation, m is the solution concentration expressed as a molality, a unit we have not discussed. For very dilute solutions, the molality m and molarity M are essentially equal,

electrolyte A solute that when dissolved in water forms a solution that conducts electricity.

nonelectrolyte A solute that when dissolved in water forms a solution that does not conduct electricity.

colligative property A solution property that depends only on the concentration of solute particles in solution.



1

Initially, equal volumes of pure water and copper sulfate solution (blue) are placed under a glass dome that prevents water vapor from escaping to the outside.



2

After some time has passed, the volume of pure water has decreased, while that of the copper sulfate solution has increased.

Figure 7.11 The vapor pressure of water above a solution is lower than the vapor pressure of pure water. Remember that pressure is a force per unit area. Think of this force as “pushing” water molecules in the vapor state, and explain the process shown in the photos.

Table 7.5 A Comparison of Colligative Properties of Pure Solvent and Solutions

Property	Pure Solvent	Solution
Vapor pressure	Normal	Lower than pure solvent
Boiling point	Normal	Higher than pure solvent
Freezing point	Normal	Lower than pure solvent

and M can be used in Equation 7.12 instead of m . This approximation will be used for calculating colligative properties of solutions in this book. The symbol Δt is the boiling point or freezing point difference between pure solvent and solution. The specific equations used to calculate Δt for boiling and freezing points are

$$\Delta t_b = nK_bM \quad (7.13)$$

$$\Delta t_f = nK_fM \quad (7.14)$$

The subscripts b and f refer to boiling or freezing, and K_b and K_f are constants characteristic of the solvent used in the solution (remember, to this point we have focused on water as the solvent). Values for K_b and K_f are given in Table 7.6 for a number of solvents. In Equations 7.13 and 7.14, M is the molarity of solute in solution, and n is the number of moles of solute particles put into solution when 1 mol of solute dissolves.

Example 7.9

Calculate the boiling and freezing points of the following solutions:

- 171 g of sugar ($C_{12}H_{22}O_{11}$) is dissolved in enough water to give 1.00 L of solution.
- 13.4 g of NH_4Cl is dissolved in water to form 500 mL of solution.

Solution

In each case, Equations 7.13 and 7.14 are used to calculate the difference between the normal boiling and freezing point of water and the solution. To use these equations, K_b and K_f are obtained from Table 7.6; the solution molarity, M , is calculated; and n is determined.

Table 7.6 Boiling and Freezing Point Constants for Various Solvents

Solvent	Normal Boiling Point ($^{\circ}C$)	K_b ($^{\circ}C/M$)	Normal Freezing Point ($^{\circ}C$)	K_f ($^{\circ}C/M$)
Benzene	80.1	2.53	5.5	4.90
Camphor			174.0	40.0
Carbon tetrachloride	76.8	5.03		
Chloroform	61.2	3.63		
Cyclohexane	81.0	2.79	6.5	20.0
Ethyl alcohol	78.5	1.22		
Water	100.0	0.52	0.0	1.86

a. To find the boiling point, calculate solution molarity.

$$(171 \text{ g } \text{C}_{12}\text{H}_{22}\text{O}_{11}) \left(\frac{1 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}}{342.0 \text{ g } \text{C}_{12}\text{H}_{22}\text{O}_{11}} \right) = 0.500 \text{ mol } \text{C}_{12}\text{H}_{22}\text{O}_{11}$$

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{0.500 \text{ mol}}{1.00 \text{ L}} = 0.500 \frac{\text{mol}}{\text{L}}$$

Determine n : Because sugar does not dissociate on dissolving, $n = 1$. Therefore,

$$\Delta t_b = nK_bM = (1)(0.52^\circ\text{C}/M)(0.500 \text{ M}) = 0.26^\circ\text{C}$$

Because boiling points are higher in solutions, we add Δt_b to the normal boiling point of water:

$$\text{solution boiling point} = 100.00^\circ\text{C} + 0.26^\circ\text{C} = 100.26^\circ\text{C}$$

To find the freezing point, calculate Δt_f :

$$\Delta t_f = nK_fM = (1)(1.86^\circ\text{C}/M)(0.500 \text{ M}) = 0.93^\circ\text{C}$$

Because freezing points are lower in solutions, we subtract Δt_f from the normal freezing point of water:

$$\text{solution freezing point} = 0.00^\circ\text{C} - 0.93^\circ\text{C} = -0.93^\circ\text{C}$$

b. Similarly,

$$(13.4 \text{ g } \text{NH}_4\text{Cl}) \left(\frac{1 \text{ mol } \text{NH}_4\text{Cl}}{53.5 \text{ g } \text{NH}_4\text{Cl}} \right) = 0.250 \text{ mol } \text{NH}_4\text{Cl}$$

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{0.250 \text{ mol}}{0.500 \text{ L}} = 0.500 \frac{\text{mol}}{\text{L}}$$

Because NH_4Cl dissociates in water, 1 mol of solute gives 2 mol of particles (ions):



Thus, we conclude that $n = 2$. Therefore,

$$\Delta t_b = nK_bM = (2)(0.52^\circ\text{C}/M)(0.500 \text{ M}) = 0.52^\circ\text{C}$$

$$\text{solution boiling point} = 100.00^\circ\text{C} + 0.52^\circ\text{C} = 100.52^\circ\text{C}$$

$$\Delta t_f = nK_fM = (2)(1.86^\circ\text{C}/M)(0.500 \text{ M}) = 1.86^\circ\text{C}$$

$$\text{solution freezing point} = 0.00^\circ\text{C} - 1.86^\circ\text{C} = -1.86^\circ\text{C}$$

Example 7.9 demonstrates the influence of solute dissociation on colligative properties. Even though the solutions in parts a and b have the same molarity, the NH_4Cl dissociates and produces twice as many solute particles in solution. Hence, it causes twice as much change in the colligative properties.

Osmotic pressure, another important colligative property, can be illustrated by some hypothetical experiments. Consider Figure 7.12, where a sugar solution is separated

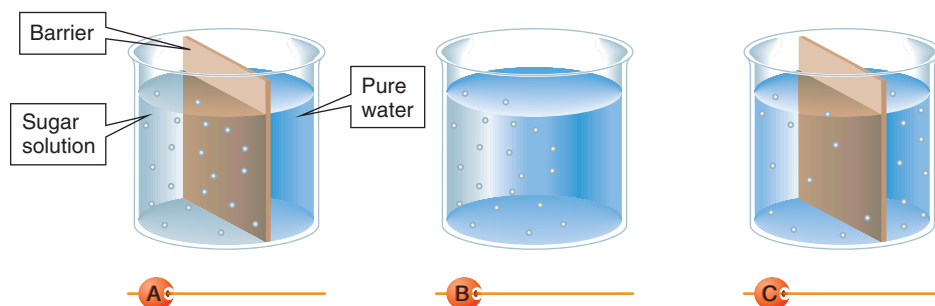


Figure 7.12 Diffusion eliminates concentration gradients.

Study Skills 7.1 Getting Started with Molarity Calculations

Knowing where to start or what to do first is a critical part of working any math-type problem. This might be a factor if molarity calculations are difficult for you. First, of course, you must identify a problem as a molarity problem. This can be done by looking for a key word or phrase (molar, molarity, or moles/liter) or the abbreviation M. Second, remember that you have a formula for molarity

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

and the problem might be treated as a formula-type problem. Look for the given numbers and their units, and see if they match the units of the formula. If they do, put them into the formula and do the calculations. For example, if you are asked to calculate the molarity of a solution that contains 0.0856 mol NaCl dissolved in enough water to give 0.100 L of solution, you could put the numbers and their units directly into the formula:

$$M = \frac{0.0856 \text{ mol NaCl}}{0.100 \text{ L solution}} = 0.856 \text{ mol NaCl/L solution}$$

However, if you must calculate the molarity of a solution that contains 5.00 g of NaCl in enough water to give 100 mL of solution, the units of the numbers do not match those of the formula. The factor-unit method can be used to convert each quantity into the units needed by the formula

$$5.00 \text{ g NaCl} \times \frac{1 \text{ mol NaCl}}{58.4 \text{ g NaCl}} = 0.0856 \text{ mol NaCl}$$

$$100 \text{ mL solution} \times \frac{1 \text{ L solution}}{1000 \text{ mL solution}} = 0.100 \text{ L solution}$$

These numbers and units can then be put into the formula

$$M = \frac{0.0856 \text{ mol NaCl}}{0.100 \text{ L solution}} = 0.856 \text{ mol NaCl/L solution}$$

Alternatively, the problem can be solved by remembering the units of the answer (molarity would have the units mol NaCl/L solution), noting the numbers and units of the given quantities (5.00 g NaCl/100 mL solution), and using the factor-unit method to convert the units of the given quantity to those of the answer:

$$\text{Step 1. } \frac{5.00 \text{ g NaCl}}{100 \text{ mL solution}}$$

$$\text{Step 2. } \frac{5.00 \text{ g NaCl}}{100 \text{ mL solution}} = \frac{\text{mol NaCl}}{\text{L solution}}$$

$$\text{Step 3. } \frac{5.00 \text{ g NaCl}}{100 \text{ mL solution}} \times \frac{1 \text{ mol NaCl}}{58.4 \text{ g NaCl}} \times \frac{1000 \text{ mL solution}}{1 \text{ L solution}} = \frac{\text{mol NaCl}}{\text{L solution}}$$

$$\text{Step 4. } \frac{(5.00)(1 \text{ mol NaCl})(1000)}{(100)(58.4)(1 \text{ L solution})} = 0.856 \frac{\text{mol NaCl}}{\text{L solution}}$$

The final answer, which has the correct units for a molarity, has been rounded to three significant figures.

from pure water by a barrier **A**. The barrier is removed, but the mixture is not stirred **B**. After a day or so, the barrier is replaced, with the results shown in **C**. These results are not surprising; the sugar has diffused throughout the mixture uniformly. It would have been very surprising if the process had not taken place.

Now consider the experiment shown in **Figure 7.13**, in which two solutions similar to those used before are separated by a semipermeable membrane, which has pores large enough to allow small molecules such as water to pass through but small enough to prevent passage by larger molecules or hydrated ions. In **Figure 7.13**, the membrane allows water molecules to pass but not sugar molecules.

In this experiment, a concentration difference between the liquids has been created, but diffusion is prevented from taking place as it did before. Water molecules move through the membrane in both directions, but sugar molecules cannot move into the pure water to equalize the concentration. As a result, the net flow of water through the membrane is into the sugar solution. This has the effect of increasing the volume of the sugar solution and decreasing its concentration to a value closer to that of the pure water. The movement of water creates a difference in liquid levels (*h*), which causes hydrostatic pressure against the membrane. This pressure increases until it becomes high enough to balance the tendency for net water to flow through the membrane into the sugar solution. From that time on, the flow of water in both directions through the membrane is equal, and the volume of liquid on each side of the membrane no longer changes. The hydrostatic pressure required to prevent the net flow of water through a semipermeable membrane into a solution is called the **osmotic pressure** of the solution. The process in which solvent molecules move

osmotic pressure The hydrostatic pressure required to prevent the net flow of solvent through a semipermeable membrane into a solution.

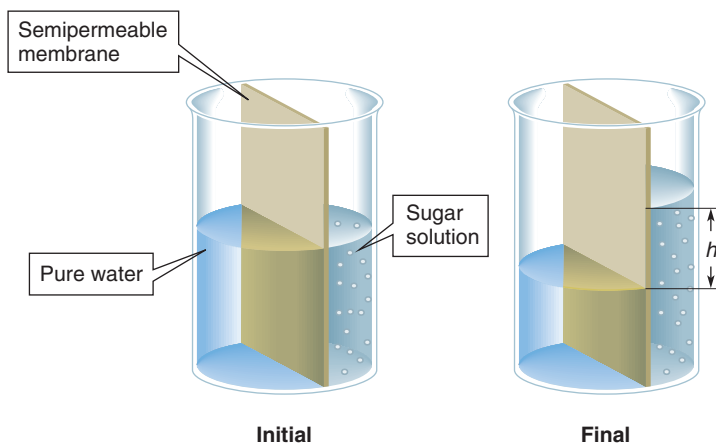


Figure 7.13 Osmosis.

through semipermeable membranes is called **osmosis**. Although our experiment doesn't illustrate it, solvent will also flow osmotically through semipermeable membranes separating solutions of different concentrations. The net flow of solvent is always from the more dilute solution into the more concentrated (see Active Figure 7.14).

The osmotic pressure that will develop across a semipermeable membrane separating pure solvent from a solution of molarity M is given by Equation 7.15, which is similar to the ideal gas law given earlier (Section 6.8):

$$\pi = nMRT \quad (7.15)$$

In this equation, π is the osmotic pressure in units that are the same as the pressure units used in the ideal gas constant R . M is the solution molarity, T is the temperature in kelvins, and n , as before, is the number of moles of solute particles obtained when 1 mol of solute dissolves. Scientists in biological and medical fields often call the product of n and M the **osmolarity** of the solution.

osmosis The process in which solvent flows through a semipermeable membrane into a solution.

osmolarity The product of n and M in the equation $\pi = nMRT$.

Example 7.10

Calculate the osmolarity and the osmotic pressure that would develop across a semipermeable membrane if the solutions of Example 7.9 were separated from pure water by the membrane. Assume a solution temperature of 27°C and use an R value of $62.4 \text{ L torr/K mol}$.

Solution

- a. The molarity of the sugar solution was found to be 0.500 mol/L . Because sugar does not dissociate, n is equal to 1, and the osmolarity nM is also equal to 0.500 mol/L .

$$\begin{aligned} \pi &= nMRT = (1) \left(0.500 \frac{\text{mol}}{\text{L}} \right) \left(\frac{62.4 \text{ L torr}}{\text{K mol}} \right) (300 \text{ K}) \\ &= 9.36 \times 10^3 \text{ torr} \end{aligned}$$

Thus, this solution would develop a pressure sufficient to support a column of mercury $9.36 \times 10^3 \text{ mm}$ high. This is equal to about 12.3 standard atmospheres of pressure (see Table 6.3 for pressure units).

- b. The molarity of this solution was also found to be 0.500 . But, because this solute dissociates into two ions, $n = 2$. This makes the osmolarity equal to $(2)(0.500 \text{ mol/L}) = 1.00 \text{ mol/L}$:

$$\begin{aligned} \pi &= nMRT = (2) \left(\frac{0.500 \text{ mol}}{\text{L}} \right) \left(\frac{62.4 \text{ L torr}}{\text{K mol}} \right) (300 \text{ K}) \\ &= 1.87 \times 10^4 \text{ torr, or about 24.6 standard atmospheres} \end{aligned}$$



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Active Figure 7.14 Osmosis through carrot membranes. The tissue of a dried shriveled carrot (left) acts as a semipermeable osmotic membrane when placed in water. After some time, the osmotic flow of water into the carrot rehydrates the carrot (right). Go to www.cengage.com/chemistry/seager or OWL to explore an interactive version of this figure.

► **Learning Check 7.8** Calculate the boiling point, freezing point, and osmotic pressure of the following solutions. Assume that the osmotic pressure is measured at 27°C.

- A 0.100 M solution of CaCl_2 in water. The CaCl_2 is a strong electrolyte.
- A 0.100 M solution of ethylene glycol in water. Ethylene glycol does not dissociate in solution.

7.8 Colloids

Learning Objective

8. Describe the characteristics of colloids.

colloid A homogeneous mixture of two or more substances in which the dispersed substances are present as larger particles than are found in solutions.

dispersing medium The substance present in a colloidal dispersion in the largest amount.

dispersed phase The substance present in a colloidal dispersion in amounts less than the amount of dispersing medium.

Tyndall effect A property of colloids in which the path of a beam of light through the colloid is visible because the light is scattered.

Like solutions, **colloids** (or colloidal dispersions) are homogeneous mixtures of two or more components in which there is more of one component than of the others. In solutions, the terms *solvent* and *solute* are used for the components, but in colloids, the terms **dispersing medium** (for solvent) and **dispersed phase** (for solute) are used.

Solute particles (in solutions) and dispersed phase particles (in colloids) cannot be seen and do not settle under the influence of gravity. However, solute particles do not scatter or reflect light, whereas dispersed phase particles do. This and other variations in properties result from the principal difference between solutions and colloids, the size of the particles making up the solute or dispersed phase. The dissolved solute in a solution is present in the form of tiny particles (small molecules or ions) that are less than about 10^{-7} cm (0.1 μm) in diameter. The dispersed phase of colloids is made up of much larger particles (very large molecules or small pieces of matter) with diameters of 10^{-7} to 10^{-5} cm (0.1–10 μm). As a result of light scattering, colloids often appear to be cloudy. When a beam of light passes through them, they demonstrate the **Tyndall effect** in which the path of the light becomes visible (► Figure 7.15).

The word *colloidal* means “gluelike,” and some colloids, including some glues, fit this description quite well. However, many, including smoke, shaving cream, and cheese, do not. Colloids are usually differentiated according to the states of the dispersing medium and dispersed phase. Some colloid types are listed in ► Table 7.7, together with examples and specific names.

Figure 7.15 The Tyndall effect.



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Tears: Solutions for Many Eye Problems



Tears are usually associated with the act of crying. However, healthy eyes are constantly bathed with tears, which constitute a sophisticated lubrication system made up of mucus, water, and oil. The tears wash away microbes and debris and help heal any damaged eye tissue.

Some individuals suffer from a condition called dry eye syndrome. The classic symptoms of this condition are a burning sensation in the eyes coupled with a scratchy or gritty feeling. Interestingly, constant tearing and watering are also symptomatic of the condition. More women than men commonly suffer from this ailment, with the onset often occurring near the time they go through menopause. This indicates a possible link between the dry eye condition and hormonal changes in the body.

Dry eye syndrome is not a cause of blindness, and often goes away on its own. However, it can seriously interfere with working, reading, driving, and other normal activities of daily life. A number of simple remedies and practices have been shown to help reduce or eliminate the troublesome symptoms. A number of over-the-counter eye drops that help lubricate the eyes and provide needed moisture are available. However, some such products that contain preservatives or materials to eliminate redness can make dry eye syndrome symptoms worse and should be avoided. Lubricating ointments applied at bedtime work well by moistening the eyes throughout the night. Other practices that help include drinking plenty of water to remain hydrated and avoiding hair dryers, electric fans, persistent winds, overheated rooms, and

exposure to smoke. Home air humidifiers have also proved to be helpful.

Anyone with eyes that continue to burn, itch, or water frequently in spite of taking appropriate precautions should consult an ophthalmologist or optometrist to determine if an infection or other serious condition is present.



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Examples of typical over-the-counter eye drops used by some to combat dry eye syndrome

Table 7.7 Types of Colloids

Colloid Type			
Dispersing Medium	Dispersed Phase	Name	Examples
Gas	Liquid	Aerosol	Fog, aerosol sprays, some air pollutants
Gas	Solid		Smoke, some air pollutants
Liquid	Gas	Foam	Whipped cream, shaving cream
Liquid	Liquid	Emulsion	Milk, mayonnaise
Liquid	Solid	Sol	Paint, ink, gelatin dessert
Solid	Gas	Solid foam	Marshmallow, pumice stone, foam rubber
Solid	Liquid		Butter, cheese
Solid	Solid		Pearls, opals, colored glass, some metal alloys

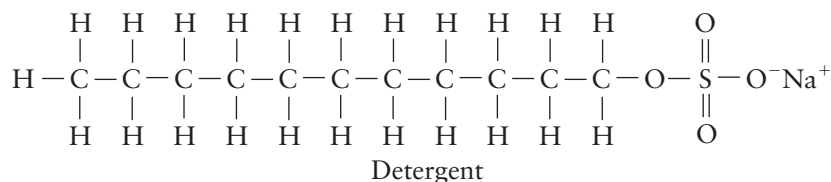
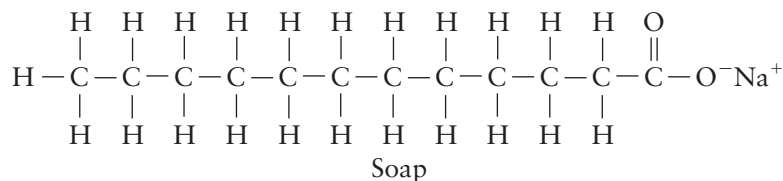
Sols that become viscous and semisolid are called *gels*. In these colloids, the solid dispersed phase has a very high affinity for the dispersing medium. The gel “sets” by forming a three-dimensional network of solid and dispersing medium. Other examples of gels are fruit jellies and “canned heat” (jellied alcohol).

Much of the interest in colloids is related to their formation or destruction. Ions that are present in the dispersing medium are attracted to colloid particles and stick on their surfaces. The charge (+ or −) of the ions depends on the nature of the colloid, but all colloid particles within a particular system will attract ions of only one charge or the other. In this way, the colloid particles all acquire the same charge and repel each other. This repulsion helps prevent the particles from coalescing into aggregates large enough to settle out.

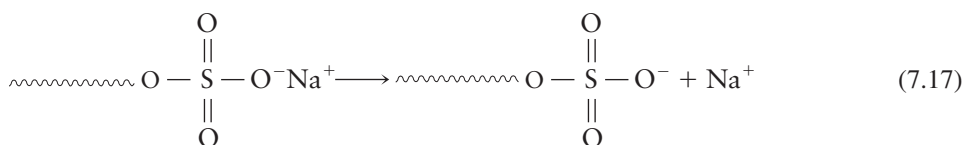
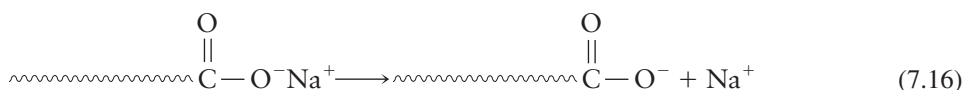
In the Cottrel precipitator, colloidal solids are removed from gaseous smokestack wastes before they are released into the atmosphere. The precipitator contains a number of highly charged plates or electrodes. As smoke passes over the charged surfaces, the colloid particles lose their charges. The particles then coalesce into larger particles that settle out and are collected for disposal.

Some colloids are stabilized (prevented from coalescing) by substances known as **emulsifying agents** or **stabilizing agents**. Mayonnaise-like salad dressing is a colloid of oil in water, with compounds from egg yolk acting as the emulsifying agent. These compounds form a coating around the oil droplets, which keeps them separated and suspended in the water.

The cleaning action of soaps and detergents comes from their activity as emulsifying agents. Both soaps and detergents contain long molecules with structures like the following:



When placed in water, soaps and detergents dissociate to form ions, as shown in Equations 7.16 and 7.17, where the long carbon chains are represented by a wavy line.



Nonpolar oils and greases are not soluble in water, but they are attracted to the uncharged ends of the soap or detergent ions. As a result of this attraction, the soap or detergent forms a charged layer around the oil droplets, which keeps them separated and suspended (see Figure 7.16). Certain compounds (lecithins) of egg yolk act in much the same way to stabilize the mayonnaise-like dressing discussed earlier.

7.9 Dialysis

Learning Objective

- Describe the process of dialysis, and compare it to the process of osmosis.

Earlier we discussed semipermeable membranes that selectively allow solvent to pass but retain dissolved solutes during osmosis. **Dialyzing membranes** are semipermeable membranes with larger pores than osmotic membranes. They hold back colloid particles

emulsifying agent (stabilizing agent) A substance that when added to colloids prevents them from coalescing and settling.

dialyzing membrane A semipermeable membrane with pores large enough to allow solvent molecules, other small molecules, and hydrated ions to pass through.



Approximately 70% of the Earth's surface is covered with water in the form of salty solutions called oceans or seas. Massive rivers of moving water flow between these oceans. One of these rivers, called the Gulf Stream, is made up of warm surface water from the South Atlantic Ocean. It flows through the North Atlantic past Europe on its way north toward Iceland. As it passes Europe, the water cools significantly, releasing heat that increases the average temperature of European countries by 5–8°C.

During its journey from the South Atlantic, the concentration of salt in the Gulf Stream water has steadily increased as a result of evaporation of some of the warm water. This increase in salt concentration coupled with the cooling of the water as it moves north causes the density of the Gulf Stream water to increase to the point that, at approximately the latitude of Iceland, it plunges into the depths and becomes a cold river flowing south along the ocean floor. As the cold salty water sinks and flows south, more warmer surface water flows north to replace it. The south-flowing cold water is eventually pushed to the surface, where it warms up and begins to evaporate, thus completing a cycle. This cycle acts as sort of a huge liquid conveyor belt that continues to cause warm surface water to flow past Europe and warm it.

The concern of climatologists is that the atmosphere of the Earth is undoubtedly warming, and the extra heat is melting ice in the Arctic ocean. The fresh water from the melting ice flows into the salty North Atlantic. If this fresh water dilutes the salty water of the Gulf Stream enough, the Gulf Stream water might not become dense enough as

it cools in the North Atlantic to sink to the ocean bottom for the return trip south. If this happens, the Gulf Stream could cease to operate, and the heat delivery to Europe would stop. Ironically, according to this possibility, global warming could result in a cooling of Europe, possibly enough to cause a European mini ice age.



An increase in the rate of breakup of glaciers (calving) as they approach the oceans is one indication of global warming.

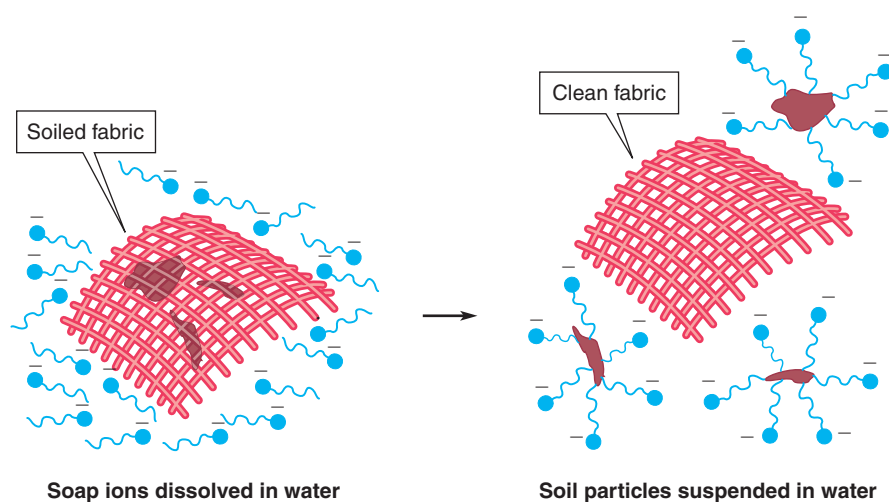


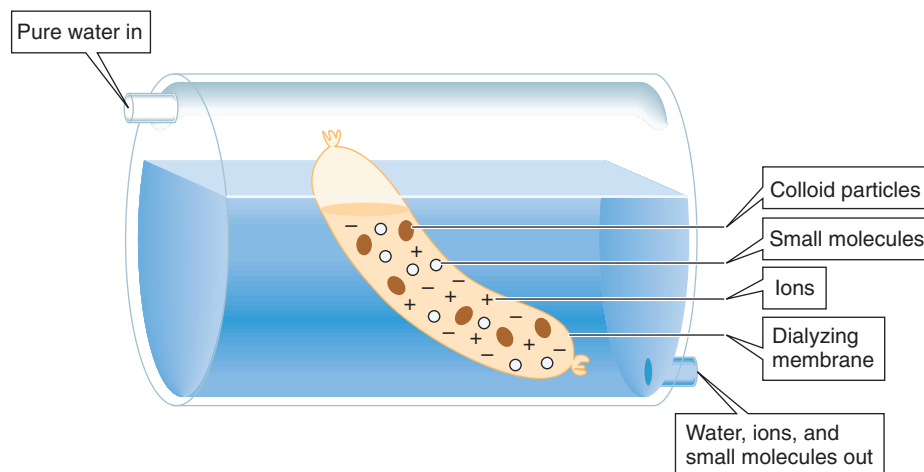
Figure 7.16 The cleaning action of soaps and detergents.

and large molecules but allow solvent, hydrated ions, and small molecules to pass through. The passage of these ions and small molecules through such membranes is called **dialysis**. Dialysis can be used to separate small particles from colloids, as shown in Figure 7.17.

A mixture containing water, ions, small molecules, and colloid particles is placed inside a bag made from a dialyzing membrane. Water flowing around the bag carries away ions and small molecules that pass through the membrane. Water molecules move through the membrane in both directions, but the colloid particles remain inside the bag.

dialysis A process in which solvent molecules, other small molecules, and hydrated ions pass from a solution through a membrane.

Figure 7.17 Dialysis. This is one method of dialysis used to purify proteins.



A similar technique is used to clean the blood of people suffering from kidney malfunction. The blood is pumped through tubing made of a dialyzing membrane. The tubing passes through a bath in which impurities collect after passing out of the blood. Blood proteins and other important large molecules remain in the blood.

Concept Summary

Physical States of Solutions. Solutions, homogeneous mixtures of a solvent and one or more solutes, can be found in any of the three states of matter: solid, liquid, or gas. The physical state of the solution is often the same as the physical state of the solvent.

Objective 1, Exercise 7.4

Solubility. The amount of solute that will dissolve in a quantity of solvent to form a saturated solution is the solubility of the solute. Solubility depends on similarities in polarities of the solvent and solute; it generally increases with temperature for solid and liquid solutes, but decreases with temperature for gaseous solutes.

Objective 2, Exercises 7.6 and 7.12

The Solution Process. The solution process of solid solute in a liquid solvent can be thought of in terms of the solvent molecules attracting the solute particles away from the solute crystal lattice. The solute is picked apart and solute particles hydrated as a result of attractions between water molecules and solute particles. Heat is generally absorbed or released when a solute dissolves in a solvent. When heat is released, the solution process is called exothermic, and the solution temperature increases. When heat is absorbed, the solution process is endothermic, and the solution cools as solute dissolves.

Objective 3, Exercise 7.16

Solution Concentrations. Relationships between the amount of solute and the amount of solution containing the solute are called concentrations. They may be expressed as molarity, weight/weight percent, weight/volume percent, or volume/volume percent.

Objective 4, Exercises 7.22b, 7.30c, 7.34a, and 7.38c

Solution Preparation. Solutions of specific concentration can be prepared by mixing appropriate amounts of solute and solvent or by diluting a more concentrated solution with solvent.

Objective 5, Exercises 7.46 and 7.48b

Solution Stoichiometry. When solution concentrations are expressed as molarities, the mole concept can be applied to reactions taking place between substances that are solutes in the solutions.

Objective 6, Exercise 7.56

Solution Properties. A number of solution properties differ from the properties of pure solvent. Ionic or highly polar solutes that dissociate in solution result in solutions that conduct electricity. Colligative solution properties depend on the concentration of solute particles in the solution and include vapor pressure, boiling point, freezing point, and osmotic pressure.

Objective 7, Exercises 7.64a & c and 7.74

Colloids. Homogeneous mixtures called colloids, or colloidal dispersions, differ from solutions in terms of the size of the dispersed phase particles. In colloids, the particles are large enough to scatter light and thus show the Tyndall effect. Colloids, like solutions, occur in all three physical states, depending primarily on the physical state of the dispersing medium. In true colloids, the suspension is permanent because dispersed particles acquire similar charges by adsorbing ions from the dispersing medium and repel each other or because emulsifying agents keep the dispersed particles from coalescing.

Objective 8, Exercise 7.82

Dialysis. Dialyzing membranes are semipermeable but with pores large enough to allow solvent molecules, hydrated ions, and small molecules to pass through in a process called dialysis. The process is important in the removal of impurities from the blood and is applied artificially for people suffering from kidney malfunction.

Objective 9, Exercise 7.84

Key Terms and Concepts

Colligative property (7.7)	Hydrated ion (7.3)	Solubility (7.2)
Colloid (7.8)	Immiscible (7.2)	Soluble substance (7.2)
Concentration (7.4)	Insoluble substance (7.2)	Solute (7.1)
Dialysis (7.9)	Molarity (M) (7.4)	Solution (7.1)
Dialyzing membrane (7.9)	Nonelectrolyte (7.7)	Solvent (7.1)
Dispersed phase (7.8)	Osmolarity (7.7)	Supersaturated solution (7.2)
Dispersing medium (7.8)	Osmosis (7.7)	Tyndall effect (7.8)
Dissolving (7.1)	Osmotic pressure (7.7)	Volume/volume percent (7.4)
Electrolyte (7.7)	Percent (7.4)	Weight/volume percent (7.4)
Emulsifying agent (stabilizing agent) (7.8)	Saturated solution (7.2)	Weight/weight percent (7.4)

Key Equations

1. Solution concentration in terms of molarity (Section 7.4):

$$M = \frac{\text{moles of solute}}{\text{liters of solution}} \quad \text{Equation 7.5}$$
2. Solution concentration in terms of weight/weight % (Section 7.4):

$$\%(w/w) = \frac{\text{solute mass}}{\text{solution mass}} \times 100 \quad \text{Equation 7.6}$$

$$\frac{\text{f solute}}{\text{milliliters of solution}} \times 100 \quad \text{Equation 7.7}$$
4. Solution concentration in terms of volume/volume % (Section 7.4):

$$\%(v/v) = \frac{\text{solute volume}}{\text{solution volume}} \times 100 \quad \text{Equation 7.8}$$
5. Dilution of concentrated solution to make less-concentrated solution (Section 7.5):


$$(C_c)(V_c) = (C_d)(V_d)$$
6. Boiling point elevation of a solution (Section 7.12):

$$\Delta t_b = nK_b M \quad \text{Equation 7.13}$$
7. Freezing point depression of a solution (Section 7.7):

$$\Delta t_f = nK_f M \quad \text{Equation 7.14}$$
8. Osmotic pressure of a solution (Section 7.7):

$$\pi = nMRT \quad \text{Equation 7.15}$$

Exercises

 **OWL** Interactive versions of these problems are assignable in OWL. Even-numbered exercises are answered in Appendix B.

Blue-numbered exercises are more challenging.

Physical States of Solutions (Section 7.1)

7.1 Many solutions are found in the home. Some are listed below, with the composition as printed on the label. When no percentage is indicated, components are usually given in order of decreasing amount. When water is present, it is often not

mentioned on the label or it is included in the inert ingredients. Identify the solvent and solutes of the following solutions:

- Antiseptic mouthwash: alcohol 25%, thymol, eucalyptol, methyl salicylate, menthol, benzoic acid, boric acid
- Paregoric: alcohol 45%, opium 0.4%
- Baby oil: mineral oil, lanolin (there happens to be no water in this solution—why?)
- Distilled vinegar: acetic acid 5%

7.2 Many solutions are found in the home. Some are listed below, with the composition as printed on the label. When no percentage is indicated, components are usually given in order of decreasing amount. When water is present, it is often not mentioned on the label or it is included in the inert ingredients. Identify the solvent and solutes of the following solutions:

- a. Liquid laundry bleach: sodium hypochlorite 5.25%, inert ingredients 94.75%
- b. Rubbing alcohol: isopropyl alcohol 70%
- c. Hydrogen peroxide: 3% hydrogen peroxide
- d. Aftershave: SD alcohol, water, glycerin, fragrance, menthol, benzophenone-1, coloring

7.3 Classify the following as being a solution or not a solution. Explain your reasons when you classify one as *not* a solution. For the ones classified as solutions, identify the solvent and solute(s).

- a. Maple syrup
- b. Milk
- c. Eyedrops
- d. Tomato juice
- e. Tap water

7.4 Classify the following as being a solution or not a solution. Explain your reasons when you classify one as *not* a solution. For the ones classified as solutions, identify the solvent and solute(s).

- a. Foggy air
- b. Tears
- c. Freshly squeezed orange juice
- d. Strained tea
- e. Creamy hand lotion

Solubility (Section 7.2)

7.5 Use the term *soluble*, *insoluble*, or *immiscible* to describe the behavior of the following pairs of substances when they are shaken together:

- a. 25 mL of water and 1 g of salt—the resulting mixture is clear and colorless.
- b. 25 mL of water and 1 g of solid silver chloride—the resulting mixture is cloudy and solid settles out.
- c. 25 mL of water and 5 mL of mineral oil—the resulting mixture is cloudy and gradually separates into two layers.

7.6 Use the term *soluble*, *insoluble*, or *immiscible* to describe the behavior of the following pairs of substances when they are shaken together:

- a. 25 mL of cooking oil and 25 mL of vinegar—the resulting mixture is cloudy and gradually separates into two layers.
- b. 25 mL of water and 10 mL of rubbing alcohol—the resulting mixture is clear and colorless.
- c. 25 mL of chloroform and 1 g of roofing tar—the resulting mixture is clear but dark brown in color.

7.7 Define the term *miscible*. It is *not* defined in the text.

7.8 Classify the following solutions as unsaturated, saturated, or supersaturated:

- a. A solution to which a small piece of solute is added, and it dissolves.
- b. A solution to which a small piece of solute is added, and much more solute comes out of solution.
- c. The final solution resulting from the process in part b.

7.9 Suppose you put 35.8 g of ammonium sulfate into a flask and add 100 g of water at 0°C. After stirring to dissolve as much solute as possible, will you have a saturated or unsaturated solution? Explain your answer. See Table 7.2.

7.10 Suppose you have a saturated solution that is at room temperature. Discuss how it could be changed into a supersaturated solution without using any additional solute.

7.11 Classify each of the following solutes into the approximate solubility categories of Table 7.3. The numbers in parentheses are the grams of solute that will dissolve in 100 g of water at the temperature indicated.

- a. boric acid, H_3BO_3 (6.35 g at 30°C)
- b. calcium hydroxide, $\text{Ca}(\text{OH})_2$ (5.35 g at 30°C)
- c. antimony(III) sulfide, Sb_2S_3 (1.75×10^{-4} g at 18°C)
- d. copper(II) chloride, CuCl_2 (70.6 g at 0°C)
- e. iron(II) bromide, FeBr_2 (109 g at 10°C)

7.12 Classify each of the following solutes into the approximate solubility categories of Table 7.3. The numbers in parentheses are the grams of solute that will dissolve in 100 g of water at the temperature indicated.

- a. barium nitrate, $\text{Ba}(\text{NO}_3)_2$ (8.7 g at 20°C)
- b. aluminum oxide, Al_2O_3 (9.8×10^{-5} g at 29°C)
- c. calcium sulfate, CaSO_4 (0.21 g at 30°C)
- d. manganese chloride, MnCl_2 (72.3 g at 25°C)
- e. lead bromide, PbBr_2 (0.46 g at 0°C)

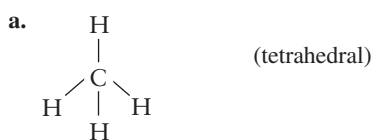
The Solution Process (Section 7.3)

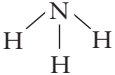
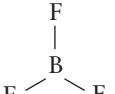
7.13 What is the difference between a nonhydrated ion and a hydrated ion? Draw a sketch using the Cl^- ion to help illustrate your answer.

7.14 Suppose you had a sample of white crystalline solid that was a mixture of barium chloride (BaCl_2) and barium sulfate (BaSO_4). Describe how you could treat the sample to isolate one of the solids in a pure state. Which solid would it be?

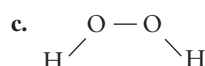
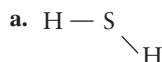
7.15 Ground-up limestone (CaCO_3) is used as a gentle abrasive in some powdered cleansers. Why is this a better choice than ground-up soda ash (Na_2CO_3)?

7.16 Indicate which of the following substances (with geometries as given) would be soluble in water (a polar solvent) and in benzene (a nonpolar solvent):

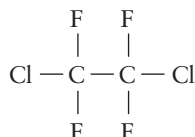


- b. Ne
- c.  (triangular-based pyramid)
- d.  (flat triangle)

7.17 Indicate which of the following substances (with geometries as given) would be soluble in water (a polar solvent) and in benzene (a nonpolar solvent):



7.18 Freons are compounds formerly used in a variety of ways. Explain why Freon-114 was useful as a degreasing agent. The molecular structure is



7.19 Suppose you put a piece of a solid into a beaker that contains water and stir the mixture briefly. You find that the solid does not immediately dissolve completely. Describe three things you might do to try to get the solid to dissolve.

Solution Concentrations (Section 7.4)

7.20 Calculate the molarity of the following solutions:

- 1.50 L of solution that contains 0.294 mol of solute.
- 200 mL of solution that contains 0.151 mol of solute.
- 0.335 mol of solute is put into a container and enough distilled water is added to give 500 mL of solution.

7.21 Calculate the molarity of the following solutions:

- 2.00 L of solution that contains 0.860 mol of solute.
- 500 mL of solution that contains 0.304 mol of solute.
- 0.115 mol of solute is put into a container and enough distilled water is added to give 250 mL of solution.

7.22 Calculate the molarity of the following solutions:

- A sample of solid NaOH weighing 4.00 g is put in enough distilled water to give 100 mL of solution.
- 20.2 g of solid CuCl_2 is dissolved in enough water to give 1.00 L of solution.
- A 10.0-mL sample of solution is evaporated to dryness and leaves 0.51 g of solid residue that is identified as KNO_3 .

7.23 Calculate the molarity of the following solutions:

- A sample of solid Na_2SO_4 weighing 0.140 g is dissolved in enough water to make 10.0 mL of solution.

- A 4.50-g sample of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is dissolved in enough water to give 150 mL of solution.
- A 43.5-g sample of K_2SO_4 is dissolved in a quantity of water, and the solution is stirred well. A 25.0-mL sample of the resulting solution is evaporated to dryness and leaves behind 2.18 g of solid K_2SO_4 .

7.24 Calculate:

- How many moles of solute is contained in 1.50 L of a 0.225 M solution?
- How many moles of solute is contained in 200 mL of a 0.185 M solution?
- What volume of a 0.452 M solution contains 0.200 mol of solute?

7.25 Calculate:

- How many moles of solute is contained in 1.25 L of a 0.350 M solution?
- How many moles of solute is contained in 200 mL of a 0.750 M solution?
- What volume of a 0.415 M solution contains 0.500 mol of solute?

7.26 Calculate:

- How many grams of solid would be left behind if 20.0 mL of a 0.550 M KCl solution was evaporated to dryness?
- What volume of a 0.315 M HNO_3 solution is needed to provide 0.0410 mol HNO_3 ?
- What volume of 1.21 M NH_4NO_3 contains 50.0 g of solute?

7.27 Calculate:

- How many grams of solid AgNO_3 will be needed to prepare 200 mL of a 0.200 M solution?
- How many grams of vitamin C ($\text{C}_6\text{H}_8\text{O}_6$) would be contained in 25.0 mL of a 1.00 M solution?
- How many moles of HCl is contained in 250 mL of a 6.0 M solution?

7.28 Calculate the concentration in % (w/w) of the following solutions. Assume water has a density of 1.00 g/mL.

- 6.5 g of sugar and 100 mL of water
- 6.5 g of any solute and 100 mL of water
- 6.5 g of any solute and 100 g of any solvent

7.29 Calculate the concentration in % (w/w) of the following solutions. Assume water has a density of 1.00 g/mL.

- 7.5 g of table salt and 100 mL of water
- 7.5 g of any solute and 100 mL of water
- 7.5 g of any solute and 100 g of any solvent

7.30 Calculate the concentration % (w/w) of the following solutions. Assume water has a density of 1.00 g/mL.

- 20.0 g of salt is dissolved in 250 mL of water.
- 0.100 mol of solid glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is dissolved in 100 mL of water.
- 120 g of solid is dissolved in 100 mL of water.
- 10.0 mL of ethyl alcohol (density = 0.789 g/mL) is mixed with 10.0 mL of water.

- 7.31** Calculate the concentration in %(w/w) of the following solutions. Assume water has a density of 1.00 g/mL.
- 5.20 g of CaCl_2 is dissolved in 125 mL of water.
 - 0.200 mol of solid KBr is dissolved in 200 mL of water.
 - 50.0 g of solid is dissolved in 250 mL of water.
 - 10.0 mL of ethyl alcohol (density = 0.789 g/mL) is mixed with 10.0 mL of ethylene glycol (density = 1.11 g/mL).
- 7.32** Calculate the concentration in %(w/w) of the following solutions:
- 20.0 g of solute is dissolved in enough water to give 150 mL of solution. The density of the resulting solution is 1.20 g/mL.
 - A 10.0-mL sample with a density of 1.10 g/mL leaves 1.18 g of solid residue when evaporated.
 - A 25.0-g sample of solution on evaporation leaves a 1.87-g residue of MgCl_2 .
- 7.33** Calculate the concentration in %(w/w) of the following solutions:
- 424 g of solute is dissolved in enough water to give 1.00 L of solution. The density of the resulting solution is 1.18 g/mL.
 - A 50.0-mL solution sample with a density of 0.898 g/mL leaves 12.6 g of solid residue when evaporated.
 - A 25.0-g sample of solution on evaporation leaves a 2.32-g residue of NH_4Cl .
- 7.34** Calculate the concentration in %(v/v) of the following solutions:
- 200 mL of solution contains 15 mL of alcohol.
 - 200-mL of solution contains 15 mL of any soluble liquid solute.
 - 8.0 fluid ounces of oil is added to 2.0 gallons (256 fluid ounces) of gasoline.
 - A solution of alcohol and water is separated by distillation. A 200-mL sample gives 85.9 mL of alcohol.
- 7.35** Calculate the concentration in %(v/v) of the following solutions:
- 250 mL of solution contains 20.0 mL of acetone.
 - 250 mL of solution contains 20.0 mL of any soluble liquid solute.
 - 1.0 quart of acetic acid is put into a 5-gallon container, and enough water is added to fill the container.
 - A solution of acetone and water is separated by distillation. A 300-mL sample gives 109 mL of acetone.
- 7.36** Consider the blood volume of an adult to be 5.0 L. A blood alcohol level of 0.50% (v/v) can cause a coma. What volume of pure ethyl alcohol, if consumed in one long drink and assumed to be absorbed completely into the blood, would result in this critical blood alcohol level?
- 7.37** The blood serum acetone level for a person is determined to be 1.8 mg of acetone per 100 mL of serum. Express this concentration as %(v/v) if liquid acetone has a density of 0.79 g/mL.
- 7.38** Calculate the concentration in %(w/v) of the following solutions:
- 200 mL of solution contains 8.00 g of Na_2SO_4 .
 - 200 mL of solution contains 8.00 g of any solute.
 - 750 mL of solution contains 58.7 g of solute.

- 7.39** Calculate the concentration in %(w/v) of the following solutions:
- 28.0 g of solute is dissolved in 200 mL of water to give a solution with a density of 1.10 g/mL.
 - A 25.0-mL solution sample on evaporation leaves a solid residue of 0.38 g.
 - On analysis for total protein, a blood serum sample of 15.0 mL is found to contain 1.02 g of total protein.
- 7.40** A saturated solution of KBr in water is formed at 20.0°C. Consult Figure 7.3 and calculate the concentration of the solution in %(w/w).
- 7.41** Assume the density of the solution prepared in Exercise 7.40 is 1.18 g/mL and express the concentration in %(w/v).

Solution Preparation (Section 7.5)

- 7.42** Explain how you would prepare the following solutions using pure solute and water. Assume water has a density of 1.00 g/mL.
- 100 mL of a 0.250 M Na_2SO_4 solution
 - 500 mL of a 0.100 M $\text{Zn}(\text{NO}_3)_2$ solution
 - 250 g of a 2.50% (w/w) NaCl solution
 - 100 mL of a 0.55% (w/v) KCl solution
- 7.43** Explain how you would prepare the following solutions using pure solute and water. Assume water has a density of 1.00 g/mL.
- 500 mL of a 2.00 M NaOH solution
 - 250 mL of a 40.0% (v/v) alcohol solution ($\text{C}_2\text{H}_5\text{OH}$)
 - 100 mL of a 10.0% (w/v) glycerol solution. Glycerol is a liquid with a density of 1.26 g/mL. Describe two ways to measure out the amount of glycerol needed.
 - Approximately 100 mL of a normal saline solution, 0.89% (w/w) NaCl
- 7.44** A solution is prepared by mixing 45.0 g of water and 15.0 g of ethyl alcohol. The resulting solution has a density of 0.952 g/mL. Express the solution concentration in %(w/w) ethyl alcohol and %(v/v) ethyl alcohol.
- 7.45** Calculate the following:
- The number of moles of NaI in 50.0 mL of a 0.400 M solution
 - The number of grams of KBr in 120 mL of a 0.720 M solution
 - The number of grams of NaCl in 20.0 mL of a 1.20% (w/v) NaCl solution
 - The number of milliliters of alcohol in 250 mL of a 20.0% (v/v) solution
- 7.46** Calculate the following:
- The number of grams of Li_2CO_3 in 500 mL of a 2.50 M Li_2CO_3 solution
 - The number of moles of NH_3 in 100 mL of a 6.00 M NH_3 solution
 - The number of milliliters of alcohol in 200 mL of a 10.8% (v/v) solution
 - The number of grams of CaCl_2 in 20.0 mL of a 3.15% (w/v) CaCl_2 solution

- 7.47** Explain how you would prepare the following dilute solutions from the more concentrated ones:
- 200 mL of 0.500 M HCl from a 6.00 M HCl solution
 - 50 mL of 2.00 M H₂SO₄ from a 6.00 M H₂SO₄ solution
 - 100 mL of normal saline solution, 0.89% (w/v) NaCl, from a 5.0% (w/v) NaCl solution
 - 250 mL of 5.00% (v/v) acetone from 20.5% (v/v) acetone
- 7.48** Explain how you would prepare the following dilute solutions from the more concentrated ones:
- 5.00 L of 6.00 M H₂SO₄ from a 18.0 M H₂SO₄ solution
 - 250 mL of 0.500 M CaCl₂ from a 3.00 M CaCl₂ solution
 - 200 mL of 1.50% (w/v) KBr from a 10.0% (w/v) KBr solution
 - 500 mL of 10.0% (v/v) alcohol from 50.0% (v/v) alcohol
- 7.49** What is the molarity of the solution prepared by diluting 25.0 mL of 0.412 M Mg(NO₃)₂ to each of the following final volumes?
- 50.0 mL
 - 120 mL
 - 1.50 L
 - 475 mL
- 7.50** What is the molarity of the solution prepared by diluting 50.0 mL of 0.195 M KBr to each of the following volumes?
- 1.50 L
 - 200 mL
 - 500 mL
 - 700 mL

Solution Stoichiometry (Section 7.6)

- 7.51** How many milliliters of 6.00 M HCl solution would be needed to react exactly with 20.0 g of pure solid NaOH?
- $$\text{HCl(aq)} + \text{NaOH(s)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$$
- 7.52** How many grams of solid Na₂CO₃ will exactly react with 250 mL of a 1.25 M HCl solution?
- $$\text{Na}_2\text{CO}_3\text{(s)} + 2\text{HCl(aq)} \rightarrow 2\text{NaCl(aq)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$$
- 7.53** How many milliliters of 0.250 M HCl would be needed to react exactly with 10.5 g of solid NaHCO₃?
- $$\text{NaHCO}_3\text{(s)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$$
- 7.54** How many milliliters of 0.250 M AgNO₃ solution will exactly react with 25.0 mL of a 0.200 M NaCl solution?
- $$\text{NaCl(aq)} + \text{AgNO}_3\text{(aq)} \rightarrow \text{NaNO}_3\text{(aq)} + \text{AgCl(s)}$$
- 7.55** How many milliliters of 0.115 M Na₂S solution will exactly react with 35.0 mL of a 0.150 M AgNO₃ solution?
- $$2\text{AgNO}_3\text{(aq)} + \text{Na}_2\text{S(aq)} \rightarrow \text{Ag}_2\text{S(s)} + 2\text{NaNO}_3\text{(aq)}$$
- 7.56** How many milliliters of 0.150 M NH₃ solution will exactly react with 30.5 mL of 0.109 M H₂SO₄ solution?
- $$2\text{NH}_3\text{(aq)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow (\text{NH}_4)_2\text{SO}_4\text{(aq)}$$
- 7.57** How many milliliters of 0.124 M NaOH solution will exactly react with 25.0 mL of 0.210 M H₃PO₄ solution?
- $$3\text{NaOH(aq)} + \text{H}_3\text{PO}_4\text{(aq)} \rightarrow \text{Na}_3\text{PO}_4\text{(aq)} + 3\text{H}_2\text{O(l)}$$

- 7.58** How many milliliters of 0.124 M NaOH solution will exactly react with 25.0 mL of 0.210 M HCl solution?
- $$\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$$
- 7.59** How many milliliters of 0.124 M NaOH solution will exactly react with 25.0 mL of a 0.210 M H₂SO₄ solution?
- $$2\text{NaOH(aq)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{Na}_2\text{SO}_4\text{(aq)} + 2\text{H}_2\text{O(l)}$$
- 7.60** Stomach acid is essentially 0.10 M HCl. An active ingredient found in a number of popular antacids is calcium carbonate, CaCO₃. Calculate the number of grams of CaCO₃ needed to exactly react with 250 mL of stomach acid.
- $$\text{CaCO}_3\text{(s)} + 2\text{HCl(aq)} \rightarrow \text{CO}_2\text{(g)} + \text{CaCl}_2\text{(aq)} + \text{H}_2\text{O(l)}$$
- 7.61** An ingredient found in some antacids is magnesium hydroxide, Mg(OH)₂. Calculate the number of grams of Mg(OH)₂ needed to exactly react with 250 mL of stomach acid (see Exercise 7.60).
- $$\text{Mg(OH)}_2\text{(s)} + 2\text{HCl(aq)} \rightarrow \text{MgCl}_2\text{(aq)} + 2\text{H}_2\text{O(l)}$$

Solution Properties (Section 7.7)

- 7.62** Before it is frozen, ice cream is essentially a solution of sugar, flavorings, etc., dissolved in water. Use the idea of colligative solution properties and explain why a mixture of ice (and water) and salt is used to freeze homemade ice cream. Why won't just ice work?
- 7.63** If you look at the labels of automotive products used to prevent radiator freezing (antifreeze) and radiator boiling, you will find the same ingredient listed, ethylene glycol. Use the idea of colligative properties to explain how the same material can prevent an automobile cooling system from freezing and boiling.
- 7.64** Calculate the boiling and freezing points of water solutions that are 1.50 M in the following solutes:
- KCl, a strong electrolyte
 - glycerol, a nonelectrolyte
 - (NH₄)₂SO₄, a strong electrolyte
 - Al(NO₃)₃, a strong electrolyte
- 7.65** Calculate the boiling and freezing points of water solutions that are 1.25 M in the following solutes:
- KBr, a strong electrolyte
 - ethylene glycol, a nonelectrolyte
 - (NH₄)₂CO₃, a strong electrolyte
 - Al₂(SO₄)₃, a strong electrolyte
- 7.66** Calculate the boiling and freezing points of the following solutions. Water is the solvent, unless otherwise indicated.
- A 0.50 M solution of urea, a nonelectrolyte
 - A 0.250 M solution of CaCl₂, a strong electrolyte
 - A solution containing 100 g of ethylene glycol (C₂H₆O₂), a nonelectrolyte, per 250 mL
- 7.67** Calculate the boiling and freezing points of the following solutions. Water is the solvent, unless otherwise indicated.
- A solution containing 50.0 g of H₂SO₄, a strong electrolyte (both Hs dissociate), per 250 mL
 - A solution containing 200 g of table sugar (C₁₂H₂₂O₁₁), a nonelectrolyte, per 250 mL
 - A solution containing 75.0 g of octanoic acid (C₈H₁₆O₂), a nonelectrolyte, in enough benzene to give 250 mL of solution

- 7.68** Calculate the osmolarity for the following solutions:
- A 0.15 M solution of glycerol, a nonelectrolyte
 - A 0.15 M solution of $(\text{NH}_4)_2\text{SO}_4$, a strong electrolyte
 - A solution containing 25.3 g of LiCl (a strong electrolyte) per liter
- 7.69** Calculate the osmolarity for the following solutions:
- A 0.25 M solution of KCl, a strong electrolyte
 - A solution containing 15.0 g of urea ($\text{CH}_4\text{N}_2\text{O}$), a nonelectrolyte, per 500 mL
 - A solution containing 50.0 mL of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), a nonelectrolyte with a density of 1.11 g/mL, per 250 mL

NOTE: In Exercises 7.70–7.79, assume the temperature is 25.0°C, and express your answer in torr, mmHg, and atm.

- 7.70** Calculate the osmotic pressure of any solution with an osmolarity of 0.250.
- 7.71** Calculate the osmotic pressure of a 0.125 M solution of Na_2SO_4 , a strong electrolyte.
- 7.72** Calculate the osmotic pressure of a 0.200 M solution of Na_2SO_4 , a strong electrolyte.
- 7.73** Calculate the osmotic pressure of a 0.300 M solution of methanol, a nonelectrolyte.
- 7.74** Calculate the osmotic pressure of a solution that contains 35.0 g of the nonelectrolyte urea, $\text{CH}_4\text{N}_2\text{O}$, per 100 mL of solution.
- 7.75** Calculate the osmotic pressure of a solution that contains 1.20 mol of CaCl_2 in 1500 mL.
- 7.76** Calculate the osmotic pressure of a solution that has a freezing point of -0.35°C .
- 7.77** Calculate the osmotic pressure of a solution that is 0.122 M in solute and has a boiling point 0.19°C above that of pure water.
- 7.78** Calculate the osmotic pressure of a solution that contains 5.30 g of NaCl and 8.20 g of KCl per 750 mL.
- 7.79** Calculate the osmotic pressure of a solution that contains 245.0 g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), a nonelectrolyte, per liter.
- 7.80** Suppose an osmotic membrane separates a 5.00% sugar solution from a 10.0% sugar solution. In which direction will water flow? Which solution will become diluted as osmosis takes place?

Colloids (Section 7.8)

- 7.81** Explain how the following behave in a colloidal suspension: dispersing medium, dispersed phase, and colloid emulsifying agent.
- 7.82** Explain why detergents or soaps are needed if water is to be used as a solvent for cleaning clothes and dishes.

Dialysis (Section 7.9)

- 7.83** Suppose you have a bag made of a membrane like that in Figure 7.17. Inside the bag is a solution containing water and dissolved small molecules. Describe the behavior of the system when the bag functions as an osmotic membrane and when it functions as a dialysis membrane.
- 7.84** Each of the following mixtures was placed in a dialysis bag like the one shown in Figure 7.17. The bag was immersed in pure

water. Which substances will pass through the bag into the surrounding water?

- NaCl solution and starch (colloid)
- Urea (small organic molecule), and starch (colloid)
- Albumin (colloid), KCl solution, and glucose solution (small organic molecule)

Additional Exercises

- 7.85** When 5.0 mL of water and 5.0 mL of rubbing alcohol are mixed together, the volume of the resulting solution is 9.7 mL. Explain in terms of molecules why the final solution volume is not 10.0 mL.
- 7.86** A student made a 7.00% (w/v) solution by dissolving 7.00 grams of sodium chloride (salt) in an appropriate volume of water. Assume the density of the water was 1.00 g/mL, and that there was no increase in volume when the salt was added to the water. Calculate the density of the resulting solution in g/mL.
- 7.87** Ethylene glycol is mixed with water and used as an antifreeze in automobile cooling systems. If a 50% (v/v) solution is made using pure ethylene glycol and pure water, it will have a freezing point of about -65°C . What will happen to the freezing point of the mixture if ethylene glycol is added until the concentration is 70% (v/v) ethylene glycol? Explain your answer.
- 7.88** How many mL of 1.50 M HCl solution contains enough HCl to react completely with 0.500 g of zinc metal? The reaction is $\text{Zn(s)} + 2\text{HCl(aq)} \rightarrow \text{ZnCl}_2\text{(aq)} + \text{H}_2\text{(g)}$.
- 7.89** At 20°C ethyl alcohol has a vapor pressure of 43.9 torr, and the vapor pressure of water at the same temperature is 17.5 torr. Suppose a 50% (v/v) solution of water and ethyl alcohol was brought to a boil and the first vapors given off were collected and condensed to a liquid. How would the percentage of alcohol in the condensed liquid compare to the percentage of alcohol in the original 50% solution (greater than, less than, equal to)? Explain your reasoning.

Allied Health Exam Connection

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- 7.90** If a salt is added to water, which of the following is likely to occur?
- The boiling point will increase and the freezing point will decrease.
 - The boiling point will increase and the freezing point will increase.
 - The boiling point will decrease and the freezing point will decrease.
 - The boiling point will decrease and the freezing point will increase.

- 7.91** A cell is in a solution in which the concentration of solutes is higher inside the cell than outside the cell. The cell will likely:
- swell up and possibly burst
 - shrivel and shrink
 - maintain its size
 - grow a cell wall for support
- 7.92** What will happen if a semipermeable membrane is placed between two different concentrations of a NaCl solution?
- The solute will move toward the higher concentration.
 - The solute will move toward the lower concentration.
 - The solvent will move toward the higher concentration.
 - The solvent will move toward the lower concentration.
- 7.93** Given a sample of $C_6H_{12}O_6(aq)$, which of the following is true?
- The glucose is the solvent and water is the solute.
 - The glucose is the solvent and water is the solvent.
 - The glucose is the solute and water is the solute.
 - The glucose is the solute and water is the solvent.
- 7.94** Which one of the following compounds is a nonelectrolyte when dissolved in water?
- KOH
 - NH_3
 - NaBr
 - $CaCl_2$
- 7.95** An example of a strong electrolyte is:
- sugar
 - calcium chloride
 - glycerin
 - boric acid
- 7.96** A solution that contains all the solute it can normally dissolve at a given temperature must be:
- concentrated
 - supersaturated
 - saturated
 - unsaturated
- 7.97** Oil and water are immiscible (do not mix) because:
- oil is polar and water is polar
 - oil is nonpolar and water is polar
 - water is nonpolar and oil is polar
 - water is nonpolar and oil is nonpolar
- 7.98** Cells that contain more dissolved salts and sugars than the surrounding solution are called:
- isotonic
 - hypertonic
 - hypotonic
 - osmosis
- 7.99** How many grams of NaOH would be needed to make 250 ml of a 0.200 M solution? (molecular weight of NaOH = 40.0)
- 8.00 g
 - 4.00 g
 - 2.00 g
 - 2.50 g
- 7.100** Ice can be melted most effectively by _____ if 1 mole is used.
- sucrose
 - calcium chloride
 - sodium chloride
 - methanol
- 7.101** Jack has 100 mL of a 12 molar solution of sulfuric acid. How much of it should he put into a graduated cylinder to make 20 mL of a 1.2 molar solution?
- 1 mL
 - 2 mL
 - 10 mL
 - 12 mL
- 7.102** How many grams of sugar are needed to make 500 ml of a 5% (weight/volume) solution of sugar?
- 20
 - 25
 - 50
 - 10
- 7.103** As water is evaporated from a solution, the concentration of the solute in the solution will:
- increase
 - decrease
 - remain the same
- 7.104** In a dilute solution of sodium chloride in water, the sodium chloride is the:
- solvent
 - solute
 - precipitate
 - reactant
- 7.105** A salt solution has a molarity of 1.5 M. How many moles of this salt are present in 2.0 L of this solution?
- 1.5 moles
 - 2.0 moles
 - 3.0 moles
 - 0.75 moles

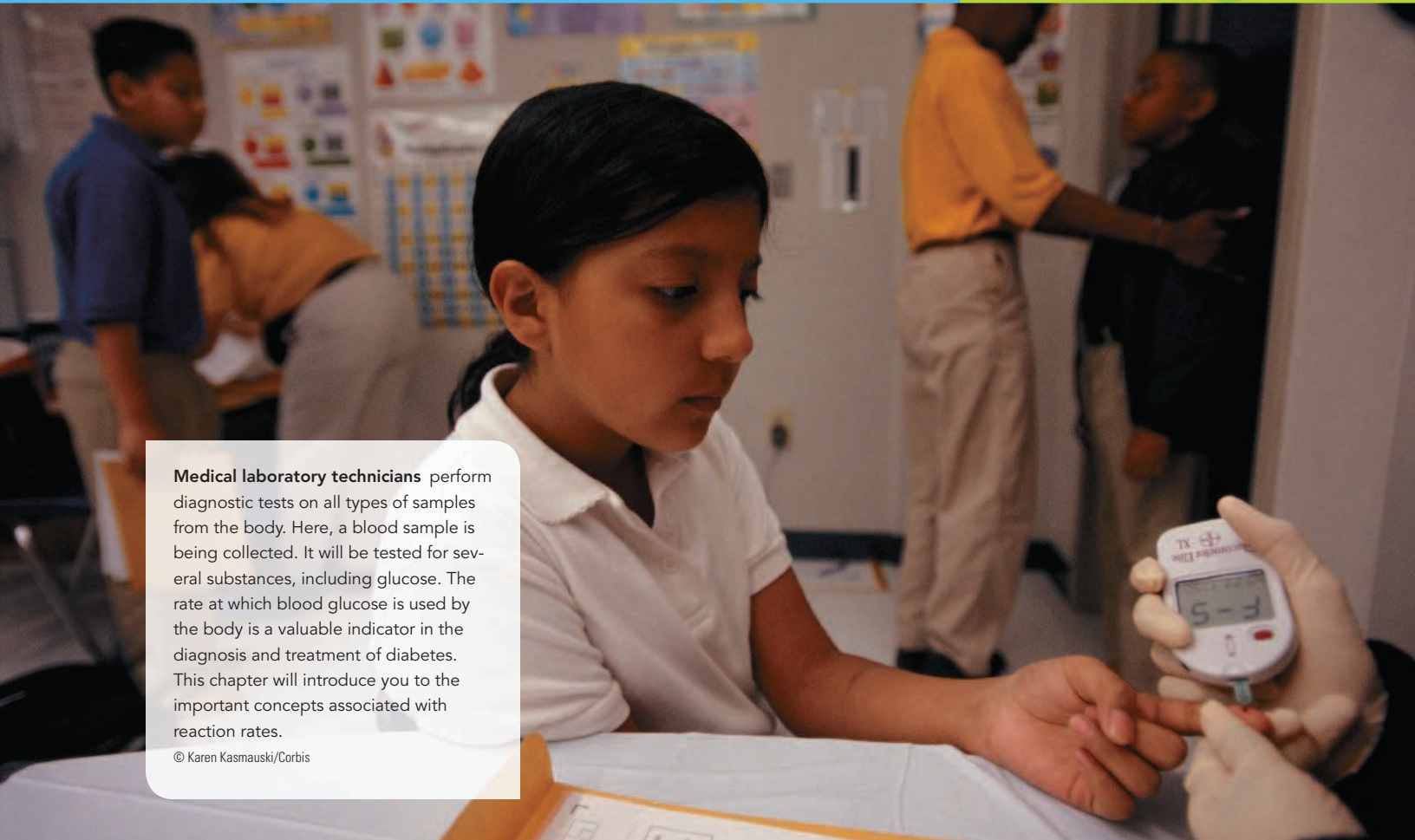
- 7.106** If 58.5 g of NaCl (1 mole of NaCl) are dissolved in enough water to make 0.500 L of solution, what is the molarity of this solution?
- 2.0 M
 - 11.7 M
 - 1.0 M
 - The answer cannot be determined from the information above.
- 7.107** To prepare 100 mL of a 0.20 M NaCl solution from a stock solution of 1.00 M NaCl, you should mix:
- 20 mL of stock solution with 80 mL of water
 - 40 mL of stock solution with 60 mL of water
 - 20 mL of stock solution with 100 mL of water
 - 25 mL of stock solution with 75 mL of water
- 7.108** If a 2.0 M solution is diluted to 0.5 M, and the final volume is 100 mL, what was the original volume?
- 400 mL
 - 200 mL
 - 50 mL
 - 25 mL
- 7.109** The number of moles of NaCl in 250 mL of a 0.300 M solution of NaCl is:
- 0.0750
 - 0.150
 - 0.250
 - 1.15
- 7.110** One liter of solution is made by dissolving 29.2 g of NaCl in water. What is the molarity of the solution?
- 0.5 M
 - 2.0 M
 - 1.3 M
 - 0.82 M
- 7.111** If a red blood cell is placed in sea water, it will be in what kind of solution?
- isotonic
 - hypotonic
 - hypertonic
 - facilitated diffusion
- 7.112** When placed in distilled water, a human red blood cell:
- shrivels up
 - neither shrinks nor swells
 - takes up more salts to balance all concentrations
 - swells to a larger size
- 7.113** The movement of substances from a lesser concentration to a higher concentration is called:
- osmosis
 - diffusion
 - active transport
 - pinocytosis
- 7.114** Primary intermolecular interactions between a K cation and H₂O molecules are:
- hydrogen bonds
 - dipole-dipole interactions
 - ion-dipole interactions
 - London forces
- 7.115** All of the following are colligative properties of solutions EXCEPT:
- vapor pressure
 - osmotic pressure
 - density
 - boiling point elevation

Chemistry for Thought

- 7.116** When a patient has blood cleansed by hemodialysis, the blood is circulated through dialysis tubing submerged in a bath that contains the following solutes in water: 0.6% NaCl, 0.04% KCl, 0.2% NaHCO₃, and 0.72% glucose (all percentages are w/v). Suggest one or more reasons why the dialysis tubing is not submerged in pure water.
- 7.117** Can the terms *saturated* and *supersaturated* be used to describe solutions made of liquids that are soluble in all proportions? Explain.
- 7.118** Refer to Figure 7.3 and propose a reason why fish sometimes die when the temperature of the water in which they live increases.
- 7.119** Small souvenir salt-covered objects are made by forming the object out of wire mesh and suspending the mesh object in a container of water from a salt lake such as the Dead Sea or Great Salt Lake. As the water evaporates, the wire mesh becomes coated with salt crystals. Describe this process using the key terms introduced in Section 7.2.
- 7.120** Refer to Figure 7.6 and answer the question. How would the solubility of sugar compare in equal amounts of hot and iced tea?
- 7.121** Refer to Figure 7.12 and explain the process as requested. Draw simple diagrams showing the initial appearance and appearance after some time for a similar experiment in which the two liquids are 0.20 M copper sulfate solution and 2.0 M copper sulfate solution. Explain your reasoning.
- 7.122** Strips of fresh meat can be preserved by drying. In one process, the strips are coated with table salt and exposed to the air. Use a process discussed in this chapter and one discussed in Chapter 6 to explain how the drying takes place.

Reaction Rates and Equilibrium

8



Medical laboratory technicians perform diagnostic tests on all types of samples from the body. Here, a blood sample is being collected. It will be tested for several substances, including glucose. The rate at which blood glucose is used by the body is a valuable indicator in the diagnosis and treatment of diabetes. This chapter will introduce you to the important concepts associated with reaction rates.

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Learning Objectives

When you have completed your study of this chapter, you should be able to:

- 1 Use the concepts of energy and entropy to predict the spontaneity of processes and reactions. (**Section 8.1**)
- 2 Calculate reaction rates from experimental data. (**Section 8.2**)
- 3 Use the concept of molecular collisions to explain reaction characteristics. (**Section 8.3**)
- 4 Represent and interpret the energy relationships for reactions by using energy diagrams. (**Section 8.4**)
- 5 Explain how factors such as reactant concentrations, temperature, and catalysts influence reaction rates. (**Section 8.5**)
- 6 Relate experimental observations to the establishment of equilibrium. (**Section 8.6**)
- 7 Write equilibrium expressions based on reaction equations, and do calculations based on equilibrium expressions. (**Section 8.7**)
- 8 Use Le Châtelier's principle to predict the influence of changes in concentration and reaction temperature on the position of equilibrium for a reaction. (**Section 8.8**)

OWL Online homework for this chapter may be assigned in OWL.

According to calculations, carbon in the form of a diamond will spontaneously change into graphite. Owners of diamonds seem unconcerned by this fact; they know from experience that their investments in gems are secure. In reality, the change does take place, but so slowly that it is not detectable over many human lifetimes. The low rate of the reaction makes the difference.

The element barium is very poisonous when it is taken into the body as barium ions (Ba^{2+}). When barium sulfate (BaSO_4) dissolves, Ba^{2+} and SO_4^{2-} ions are formed. However, suspensions of solid BaSO_4 are routinely swallowed by patients undergoing diagnostic X-ray photography of the stomach and intestinal tract. The patients are not affected because very little BaSO_4 dissolves in the body. This lack of solubility is an equilibrium property of BaSO_4 .

8.1 Spontaneous and Nonspontaneous Processes

Learning Objective

1. Use the concepts of energy and entropy to predict the spontaneity of processes and reactions.

Years ago, tourists in Salt Lake City visited “gravity hill,” where an optical illusion made a stream of water appear to flow uphill. The fascination with the scene came from the apparent violation of natural laws—everyone knew that water does not flow uphill. Processes that take place naturally with no apparent cause or stimulus are called **spontaneous processes**. Nonspontaneous processes take place only as the result of some cause or stimulus. For example, imagine you are in the positions depicted in Figure 8.1 and want to move a boulder.

In **A**, the boulder will roll down the hill as soon as you release it; the process begins and takes place spontaneously. In **B**, you must push the boulder a little to get it over the hump, but once started, the boulder spontaneously rolls downhill. Situation **C** is very different. You must continually push on the boulder, or it will not move up the hill; at no time can you stop pushing and expect the boulder to continue moving up. The process is nonspontaneous; it takes place only because of the continuous application of an external stimulus.

As the boulder rolls downhill, it gives up energy; it moves from a state of high potential energy to a lower one. As you push the boulder uphill, it gains energy (from you). Processes that give up energy are called **exergonic** (energy out), whereas those that gain energy are called **endergonic** (energy in). Very often, energy changes in chemical processes involve heat. Those changes that do are referred to as either exothermic (heat out) or endothermic (heat in), two terms you have encountered before (Sections 5.8 and 6.11).

spontaneous process A process that takes place naturally with no apparent cause or stimulus.

exergonic process A process that gives up energy as it takes place.

endergonic process A process that gains or accepts energy as it takes place.

Figure 8.1 The problem of moving a boulder.

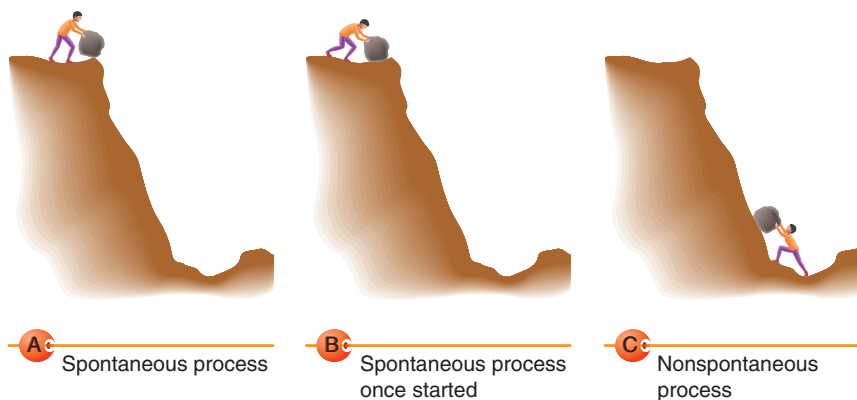




Figure 8.2 Entropy is an indicator of randomness. The mixture on the right has higher entropy (more randomness, or mixed-up character) than the mixture on the left.

Many spontaneous processes give up energy. A piece of wood, once ignited, spontaneously burns and liberates energy as heat and light. At normal room temperature, steam spontaneously condenses to water and releases heat. However, some spontaneous processes take place and either give up no energy or actually gain energy. These spontaneous processes are always accompanied by another change called an entropy increase. **Entropy** describes the disorder or mixed-up character (randomness) of a system (see [Figure 8.2](#)). Thus, an entropy increase accompanies all spontaneous processes in which energy remains constant or is gained. A drop of ink placed in a glass of water will eventually become uniformly distributed throughout the water, even though the water is not stirred. No energy change accompanies the diffusion of the ink, but the distribution of ink throughout the water is a more disorderly (higher-entropy) state than when the ink is all together in a single drop. Ice melts spontaneously at 20°C and in the process absorbs heat. The process takes place because the random distribution of water molecules in the liquid is a higher-entropy state than the orderly molecular arrangement found in crystalline ice.

Energy and entropy changes influence the spontaneity of processes in several ways:

1. A process will always be spontaneous if the energy decreases and the entropy increases. An example of such a process is the burning of a piece of wood in which heat is given up and the gaseous products of combustion are distributed throughout the surroundings, providing the entropy increase.
2. When a spontaneous process is accompanied by an energy increase, a large entropy increase must also occur. Thus, when ice spontaneously melts at 20°C , the increase in entropy is large enough to compensate for the increase in energy that also takes place.
3. A spontaneous process accompanied by an entropy decrease must also be accompanied by a compensating energy decrease. Thus, when water spontaneously freezes at 0°C , the energy loss compensates for the entropy decrease that occurs as the water molecules assume the well-ordered arrangement in ice.

It is useful to think of energy and entropy changes in terms of the directions favoring spontaneity and the directions not favoring spontaneity. It is apparent from the preceding discussion that spontaneity is favored by an energy decrease and/or an entropy increase. Processes in which one of these factors changes in a nonspontaneous direction will be spontaneous only if the other factor changes in a spontaneous direction by a large enough amount to compensate for the nonspontaneous change. The influences listed under 2 and 3 above are examples of this.

Substances that do not undergo spontaneous changes are said to be **stable**. However, stability depends on the surrounding conditions, and a change in those conditions might cause a nonspontaneous process to become spontaneous. Ice is a stable solid at -10°C and 760 torr pressure but spontaneously melts to a liquid at 5°C and 760 torr. Wood is stable

entropy A measurement or indication of the disorder or randomness of a system. The more disorderly a system is, the higher its entropy.

stable substance A substance that does not undergo spontaneous changes under the surrounding conditions.

at room temperature but spontaneously burns when its temperature equals or exceeds the ignition temperature. In the following discussions, the surrounding conditions are assumed to be those normally encountered. Otherwise, the differences are specified.

8.2 Reaction Rates

Learning Objective

2. Calculate reaction rates from experimental data.

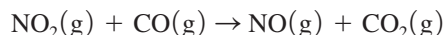
The speed of a reaction is called the **reaction rate**. It is determined experimentally as the change in concentration of a reactant or product divided by the time required for the change to occur. This average rate is represented for changes in product concentration by Equation 8.1:

$$\text{Rate} = \frac{\Delta C}{\Delta t} = \frac{C_t - C_0}{\Delta t} \quad (8.1)$$

where the delta symbol (Δ) stands for change. C_t and C_0 are the concentrations of a product at the end and beginning, respectively, of the measured time change, Δt . The time can be measured in any convenient unit.

Example 8.1

The gases NO_2 and CO react as follows:



Calculate the average rate of the reaction if pure NO_2 and CO are mixed and after 50.0 seconds the concentration of CO_2 is found to be 0.0160 mol/L.

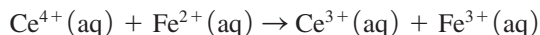
Solution

Because the reaction was started by mixing pure NO_2 and CO , the initial concentration C_0 of CO_2 was 0.000 mol/L. After 50.0 seconds, the concentration C_t of CO_2 was 0.0160 mol/L.

$$\text{Rate} = \frac{C_t - C_0}{\Delta t} = \frac{0.0160 \text{ mol/L} - 0.000 \text{ mol/L}}{50.0 \text{ s}} = 3.2 \times 10^{-4} \frac{\text{mol/L}}{\text{s}}$$

The answer is read 3.2×10^{-4} mole per liter per second. It means that during the 50.0-second time interval, an average of 3.2×10^{-4} mol CO_2 was formed in each liter of reacting mixture each second.

- **Learning Check 8.1** The Ce^{4+} and Fe^{2+} ions react in solution as follows:



Solutions of Ce^{4+} and Fe^{2+} are mixed and allowed to react. After 75.0 seconds, the concentration of Ce^{3+} is found to be 1.50×10^{-5} mol/L. Calculate the average rate of the reaction.

8.3 Molecular Collisions

Learning Objective

3. Use the concept of molecular collisions to explain reaction characteristics.

Chemical equations such as those in Example 8.1 and Learning Check 8.1 are useful in identifying reactants and products and in representing the stoichiometry of a reaction. However, they indicate nothing about how a reaction takes place—how reactants get

reaction rate The speed of a reaction.

Timed-Release Medications



Most of us have experienced the inconvenience of having to take repeated doses of a medication at specific intervals; this dosing maintains an effective level of the medication in the body throughout the day. In 1961, the first commercial attempt was made to overcome this inconvenience when the decongestant Contac® became available in the form of timed-release capsules. The approach used to time the release was simple. Each capsule contained many tiny beads of medication. Each bead was coated with a slow-dissolving polymer, but the thickness of the polymer coating was not the same on all beads. Beads with a thin coating dissolved rapidly, while those with a thicker coating dissolved more slowly. By including an appropriate mix of beads with coatings of different thickness in each capsule, a gradual, steady release of medication over a specific time period was achieved.

This same method for timed-release is still used in some products, but other methods have also been developed. The modern technology is used not only to provide a steady release of medication, but also to control the point of release in the digestive tract. Some medications are known to irritate and damage the stomach lining, or to be destroyed by the acidic environment of the stomach. An *enteric coating* that is stable in acid but that dissolves in the more basic environment of the small intestine is used to allow tablets or caplets of such materials to

pass through the stomach and release their medication in the intestines.

In a pharmacy, products in the following categories can be found with enteric coatings or in timed-release forms that claim to provide effective levels of medication for periods ranging from 6 to 24 hours: analgesics (pain relievers), allergy treatments, cold/flu remedies, laxatives, sleeping aids, gas-relief medications, appetite-control materials, diuretics (water pills), and tablets to prevent sleeping.



© Maren Slabaugh

A wide variety of products is available in timed-release form.

together (or break apart) to form products. The explanation of how a reaction occurs is called a **reaction mechanism**. Reaction mechanisms are not discussed much in this book, but most are based on the following assumptions:

1. Reactant particles must collide with one another in order for a reaction to occur.
2. Particles must collide with at least a certain minimum total amount of energy if the collision is to result in a reaction.
3. In some cases, colliding reactants must be oriented in a specific way if a reaction is to occur.

The validity of the first assumption is fairly obvious. Two molecules cannot react with each other if they are far apart. In order to break bonds, exchange atoms, and form new bonds, they must come in contact. There are, however, some exceptions, such as decompositions in which molecules break into fragments and processes in which molecules react by an internal rearrangement of their atoms.

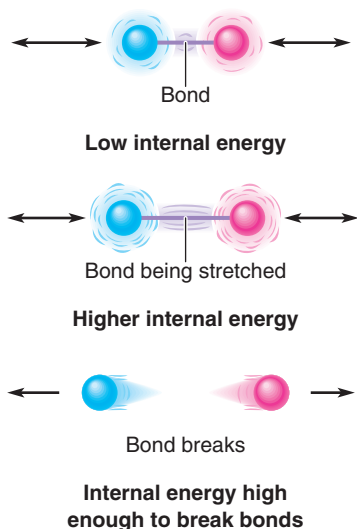
In general, reactions take place more rapidly in the gaseous or liquid state than in the solid state. This observation verifies the first assumption because molecules of gases and liquids move about freely and can undergo many more collisions than can the rigidly held molecules of solids. Reactions involving solids usually take place only on the solid surface and therefore involve only a small fraction of the total molecules present in the solid. As the reaction proceeds and the products dissolve, diffuse, or fall from the surface, fresh solid is exposed. In this way, the reaction proceeds into the solid. The rusting of iron is an example of such a process.

If collisions were the only factor, however, most gaseous and liquid state reactions would take place almost instantaneously if every collision resulted in a reaction. Such high reaction rates are not observed, a fact that brings us to assumptions 2 and 3.

One of the ways to speed up a chemical reaction is to add energy in the form of heat. The added heat increases both the average speed (kinetic energy) and the internal energy of the molecules. **Internal energy** is the energy associated with molecular vibrations.

reaction mechanism A detailed explanation of how a reaction actually takes place.

internal energy The energy associated with vibrations within molecules.



Active Figure 8.3 The internal energy of molecules. Go to www.cengage.com/chemistry/seager or OWL to explore an interactive version of this figure.

activation energy Energy needed to start some spontaneous processes. Once started, the processes continue without further stimulus or energy from an outside source.

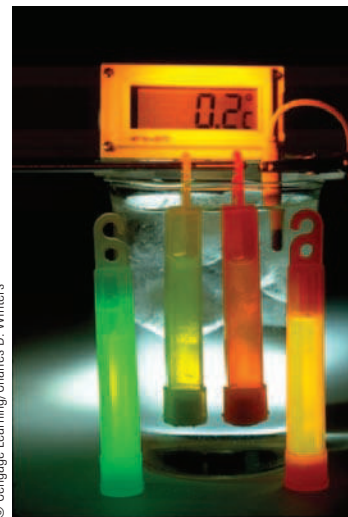
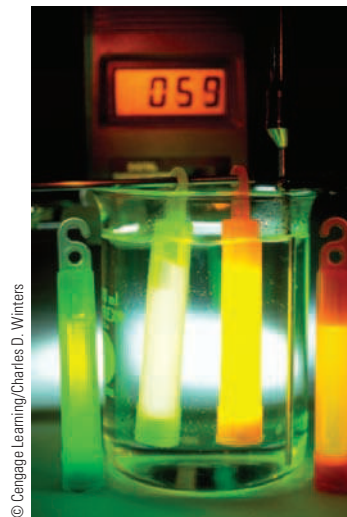


Figure 8.4 The reaction that makes a Cyalume™ light stick glow takes place more rapidly in hot water (left) than in ice water (right). The light sticks outside the container are at room temperature. Which pair of sticks would glow for a longer time? Explain your reasoning.

An increase in internal energy increases the amplitude of molecular vibrations and, if large enough, breaks bonds (see ▶ Active Figure 8.3). Internal energy is also increased by the conversion of some kinetic energy into internal energy during collisions. When heat is added, both the kinetic and the internal energy of molecules is increased. This increases the frequency and speed of collisions and the chances that a collision will cause a sufficient increase in internal energy to break bonds and bring about a reaction (see ▶ Figure 8.4).

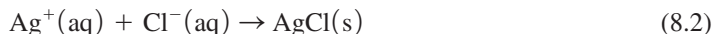
In some reaction mixtures, the average total energy of the molecules is too low at the prevailing temperature for a reaction to proceed at a detectable rate; the reaction mixture is stable. However, some reactions can be started by providing **activation energy**. Once the reaction is started, enough energy is released to activate other molecules and keep the reaction going at a good rate. The energy needed to get the boulder over the small hump in Figure 8.1B is a kind of activation energy. In many chemical reactions, activation energy causes bonds in reactant molecules to break. When the broken bonds react to form the new bonds of the products, energy is released that can cause bonds in more reactant molecules to break and the reaction to continue. The striking of a kitchen match is a good example. Activation energy is provided by rubbing the match head against a rough surface. Once started, however, the match continues to burn spontaneously.

A number of gases are routinely used in hospitals. Some of these form very flammable or even potentially explosive mixtures. Cyclopropane, a formerly used anesthetic, will burn vigorously in the presence of the oxygen in air. However, a mixture of the two will not react unless activation energy is provided in the form of an open flame or a spark. This is the reason that extreme precautions are taken to avoid open flames and sparks in a hospital operating room. Even sparks from static electricity can set off such gaseous mixtures, so special materials are used in clothing, floor coverings, and so on to prevent static electricity from building up.

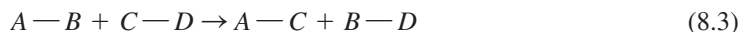
Oxygen gas does not burn, but it reacts with anything that is combustible. Oxygen is often used in hospitals in concentrations much higher than the 20% found in air. Thus, precautions must be taken to prevent fire or sparks in any areas where oxygen gas is used in high concentrations.




Orientation effects are related to which side or end of a particle actually hits another particle during a collision. Orientation effects are unimportant in many reactions.

For example, the orientation of silver ions (Ag^+) and chloride ions (Cl^-) toward each other during a collision has no effect on the rate of forming AgCl :



The reason is that Ag^+ and Cl^- are both essentially spherical charged particles. However, collision orientation may be important in reactions that involve nonspherical molecules (assumption 3). Consider the following hypothetical reaction:





It is clear that the collision orientation of $\text{A}-\text{B}$ and $\text{C}-\text{D}$ shown in  Figure 8.5A is more favorable to reaction than the orientations shown in  and .

8.4 Energy Diagrams

Learning Objective

4. Represent and interpret the energy relationships for reactions by using energy diagrams.

Energy relationships for reactions can be represented by energy diagrams like the one in  Figure 8.6. Notice the similarity to the earlier example of rolling boulders.


The energy diagrams for most reactions look generally alike, but there are some differences. Typical diagrams for exothermic (exergonic) and endothermic (endergonic) reactions are given in  Figure 8.7. It is clear that the products of exothermic reactions have lower energy than the reactants and that the products of endothermic reactions have higher energy than the reactants. When exothermic reactions occur, the energy difference between reactants and products is released. This energy often appears as heat, so heat is given up to the surroundings. When endothermic reactions occur, the energy (heat) added to the products is absorbed from the surroundings. Also, different reactions generally have different activation energies, a fact easily represented by energy diagrams.

White phosphorus, a nonmetallic element, spontaneously bursts into flame if left in a rather warm room (34°C):



Sulfur, another nonmetallic element, will also burn, but it does not ignite until heated to about 232°C :



The different activation energies for these two exothermic reactions are represented in  Figure 8.8.

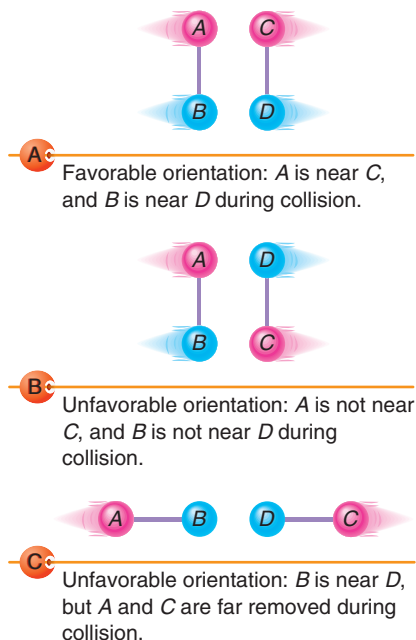
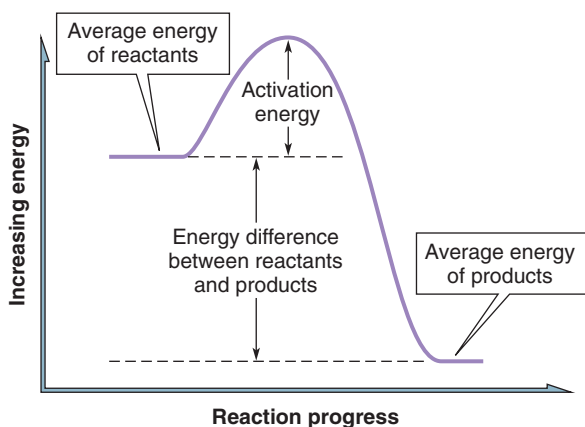
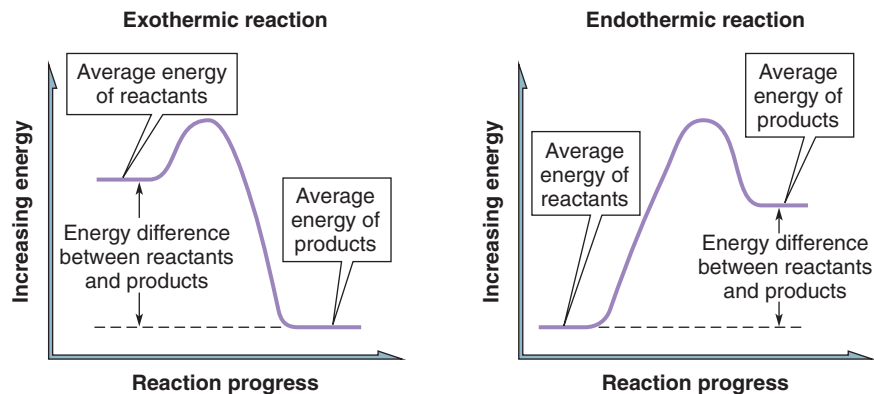


Figure 8.5 Molecular orientations during collisions.

Figure 8.6 A typical energy diagram for chemical reactions.

Figure 8.7 Energy diagrams for exothermic and endothermic reactions.



It should now be clear why we stressed the notion that some substances that are “stable” at normal living conditions undergo spontaneous changes at other conditions. It is simply that a higher temperature would provide the necessary activation energy. In a room hotter than 232°C , for example, both white phosphorus and sulfur would be “unstable” in the presence of oxygen.

8.5 Factors That Influence Reaction Rates

Learning Objective

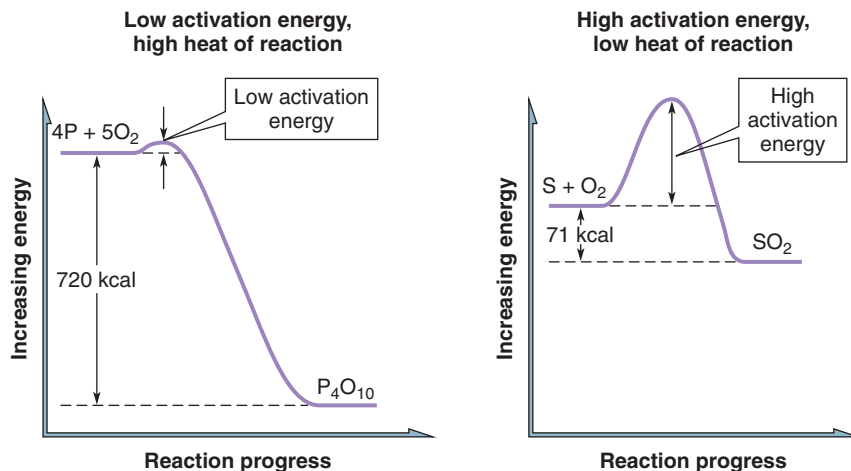
5. Explain how factors such as reactant concentrations, temperature, and catalysts influence reaction rates.

Reaction rates are influenced by a number of different factors. Four factors that affect the rates of all reactions are:

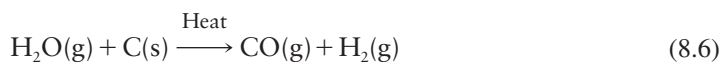
1. The nature of the reactants.
2. The concentration of the reactants.
3. The temperature of the reactants.
4. The presence of catalysts.

The formation of insoluble AgCl by mixing together solutions containing Ag^{+} and Cl^{-} ions is represented by Equation 8.2, given earlier. The white solid AgCl forms the instant the two solutions are mixed. This behavior is typical of reactions involving ionic reactants. The high reaction rate results from the attraction of the charged reactants to

Figure 8.8 Differences in activation energies.



each other. In contrast, reactions that require covalent bonds to be broken or formed often proceed slowly. The production of water gas, a mixture of hydrogen (H₂) and carbon monoxide (CO), is a reaction involving covalent bonds:



In addition, other structural characteristics of reactants, such as bond polarity or molecular size, may also be important factors in reaction rates.

The influence of reactant concentration on reaction rates can be illustrated by using the concept of molecular collisions. Suppose a reaction takes place between the hypothetical molecules *A* and *B*, which are mixed in a 1:1 ratio. The proposed reaction is



Collisions with the capability to cause a reaction to occur are called **effective collisions**. Only collisions between *A* and *B* molecules can be classified as effective, since collisions between two *A* molecules or between two *B* molecules cannot possibly yield products. Imagine the reaction is begun with two *A* molecules and two *B* molecules as shown in **Figure 8.9A**. The example is simplified by looking only at the collisions of a single *A* molecule. Initially, two of every three collisions of the *A* molecule will be effective (**A**). On doubling the number (concentration) of *B* molecules, the number of effective collisions also doubles, and four of every five collisions is effective (**B**).

When larger numbers of molecules are used, the results approach more closely those actually observed experimentally for simple chemical reactions. Imagine a mixture containing 1000 *A* molecules and 1000 *B* molecules. On the average, 1000 out of every 1999 collisions of a single *A* molecule will involve a *B* molecule. (Each *A* molecule has almost a 50–50 chance of bumping into a *B* molecule.) This gives essentially a 1:1 ratio of effective to noneffective collisions. When the number of *B* molecules is doubled to 2000, the ratio becomes 2:1, because 2000 of every 2999 collisions will be effective. Therefore, the reaction rate should double when the concentration of one reactant is doubled. This result has been verified in numerous chemical reactions. Thus, higher concentrations produce a larger number of effective collisions in a given period of time, and this increases the reaction rate.

Gas-phase reactions are easily visualized this way, but reacting liquids and solids must be looked at differently. A large piece of solid contains a large number of molecules, but, as described before, only those on the surface can react with the molecules of another substance. For this reason, the total amount of solid in a sample is not as important as the surface area of solid in contact with other reactants. The effective concentration of a solid therefore depends on its surface area and state of division. A 100-pound sack of flour is difficult to burn when it is in a single pile. The same 100 pounds, dispersed in the air as a fine dust, burns very rapidly, and a dust explosion results (see **Figure 8.10**). The effective concentrations of reacting liquids must be thought of in a similar way unless the reactants are completely miscible.

The effect of reactant temperature on reaction rates can also be explained by using the molecular collision concept. As was noted earlier, an increase in the temperature of a system increases the average kinetic energy and internal energy of the reacting molecules. The increased molecular speed (kinetic energy) causes more collisions to take place in a given time. Also, because the kinetic and internal energies of the colliding molecules are greater, a larger fraction of the collisions will be effective because they will provide the necessary activation energy.

As a rough rule of thumb, it has been found that the rate of a chemical reaction doubles for every 10°C increase in temperature. The chemical reactions of cooking take place faster in a pressure cooker because of a higher cooking temperature (Section 6.13). Also, cooling or freezing is used to slow the chemical reactions involved in the spoiling of food, souring of milk, and ripening of fruit.

effective collision A collision that causes a reaction to occur between the colliding molecules.

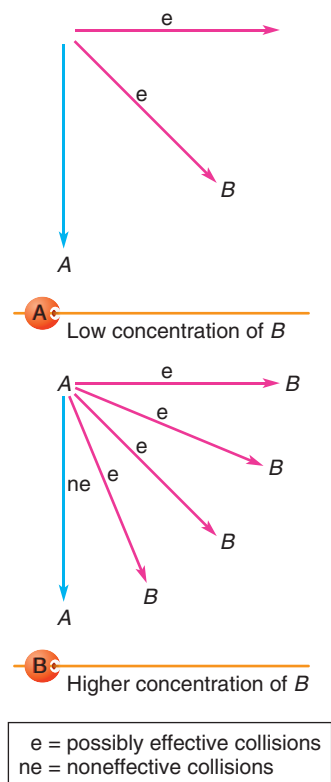


Figure 8.9 The effect of concentration on reaction rates.



1 A compact pile of lycopodium powder burns sluggishly.

2 A similar sample of lycopodium powder in a blowpipe.

3 The blown powder burns instantly with a bright flash.

Figure 8.10 Surface area influences reaction rates of solids. What is the other reactant in this reaction? How finely divided is it?

catalyst A substance that changes (usually increases) reaction rates without being used up in the reaction.

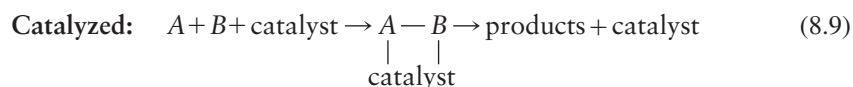
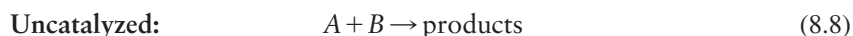
inhibitor A substance that decreases reaction rates.

homogeneous catalyst A catalytic substance that is distributed uniformly throughout the reaction mixture.

heterogeneous or surface catalyst A catalytic substance normally used in the form of a solid with a large surface area on which reactions take place.

Catalysts are substances that change reaction rates without being used up in the reactions. Usually the term *catalyst* is used to describe substances that speed up reactions. Substances that slow reactions are known as **inhibitors**. Catalysts are used in a number of different forms. Those dispersed uniformly throughout a reaction mixture in the form of individual ions or molecules are called **homogeneous catalysts**. **Heterogeneous or surface catalysts** are used in the form of solids; usually they have large surface areas on which reactions take place readily.

Catalysts enhance a reaction rate by providing an alternate reaction pathway that requires less activation energy than the normal pathway. This effect is represented by Figure 8.11. According to some theories, a catalyst provides the lower-energy pathway by entering into a reaction and forming an intermediate structure, which then breaks up to produce the final products and regenerate the catalyst:



Intermediate structure

According to another proposed mechanism, solid catalysts provide a surface to which reactant molecules become attached with a particular orientation. Reactants attached to these surfaces are sufficiently close to one another and oriented favorably enough to allow the reaction to take place. The products of the reaction then leave the surface and make the attachment sites available for catalyzing other reactant molecules.

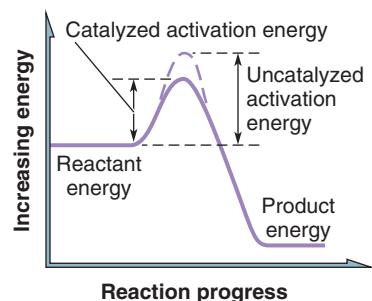


Figure 8.11 The effect of catalysts on activation energy.

8.6 Chemical Equilibrium

Learning Objective

6. Relate experimental observations to the establishment of equilibrium.

So far, the focus has been only on the reactants of a reaction. However, all reactions can (in principle) go in both directions, and the products can be looked on as reactants. Suppose equal amounts of gaseous H_2 and I_2 are placed in a closed container and allowed to react and form HI . Initially, no HI is present, so the only possible reaction is



Hypothermia: Surviving the Big Chill



The chemical reactions that maintain life in a healthy, human body take place at or near the normal body temperature of 98.6°F or 37.0°C. These reactions, like all chemical reactions, slow down as the temperature decreases. If a person's temperature decreases to a level 2°C (4°F) lower than this normal value, the person is said to be suffering from hypothermia. Death is a significant possibility if hypothermia persists for more than a few hours, and anyone whose body temperature drops lower than 32°C (90°F) has a 17–33% chance of dying.

Hypothermia occurs when the amount of heat lost by the body to the surroundings exceeds the amount of heat generated by the body as a result of such things as exercise (muscular movement) or exothermic chemical reactions associated with metabolism. The body loses heat to the surroundings by several processes including radiation, conduction, evaporation and convection. Even though it is not visible to the naked eye, heat is radiated from uncovered parts of the warm body in the form of infrared light. Because it is constantly supplied with a large amount of warm blood, an uncovered head loses large amounts of heat to the surroundings by this mechanism. Conduction is the flow of heat from a warm object, such as an ungloved hand, that touches a cooler object, such as a cold piece of wood or metal. The evaporation of perspiration is a well-known natural way for the body to cool itself in warm weather. However, the evaporation of water from clothing that has accidentally become wet in very cold weather can result in severe and dangerous heat loss from the body. Convection is a term used to describe the circulation or movement of liquids or gases. In still air, a thin layer of warm air forms near the surface of the body and creates a warm, surrounding shell. But if a breeze or wind is blowing, or the body is moving as during running, the air passing over the body removes this warm layer, and its contained heat is lost to the surroundings. This cooling by convection is the basis for windchill charts that show a lower effective temperature in the winter when the wind is blowing than when the wind is not blowing, even though the actual air temperature is the same.

Heat can be lost from the body by various combinations of these four processes. The act of exhaling air on a cold day is an example in which all four are involved. Inhaled cold, dry air is heated in the warm moist environment of the lungs by a combination of radiation, conduction, convection and evaporation. When this heated, moist air

is exhaled, a significant amount of heat is lost to the surrounding cold air.

Anyone can suffer hypothermia and even death if exposed to extreme cold long enough without adequate protection. However, the elderly are especially susceptible to hypothermia, even in less extreme conditions. There are two primary reasons for this. First, the aging body becomes progressively less able to respond to cold surroundings and maintain an even temperature. Second, the body mechanism that normally detects a drop in body temperature gradually loses its sensitivity as the body ages. As a result of these factors, some elderly individuals suffering from hypothermia do not realize they are dangerously cold, and might even die without warning.

The symptoms of hypothermia that should be watched for, especially in the elderly, are lack of interest, indifference, despondency, drowsiness, mental confusion and pallor. Prevention, of course, is the best treatment, but if hypothermia is suspected, sudden warming should not be attempted. The individual should be warmed up slowly, and professional medical help should be obtained quickly, especially if the victim is elderly.



The metallic coated wrap around this victim minimizes further cooling by preventing water evaporation from his wet clothing.

However, after a short time, some HI molecules are produced. They can collide with one another in a way that causes the reverse reaction to occur:



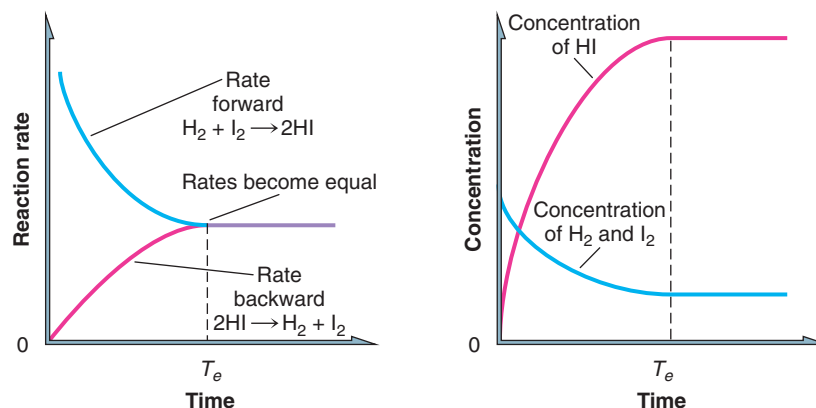
The low concentration of HI makes this reaction slow at first, but as the concentration increases, so does the reaction rate. The rate of Reaction 8.10 decreases as the concentrations of H_2 and I_2 decrease. Eventually, the concentrations of H_2 , I_2 , and HI in the reaction mixture reach levels at which the rates of the forward (Equation 8.10) and reverse (Equation 8.11) reactions are equal. From that time on, the concentrations of H_2 , I_2 , and HI in the mixture remain constant, since both reactions take place at the same rate and each substance is being produced as fast as it is used up. When the forward and reverse reaction rates are equal, the reaction is in a **state of equilibrium**, and the concentrations are called **equilibrium concentrations**.

The behavior of reaction rates and reactant concentrations for both the forward and reverse reactions is shown graphically in Figure 8.12.

state of equilibrium A condition in a reaction system when the rates of the forward and reverse reactions are equal.

equilibrium concentrations The unchanging concentrations of reactants and products in a reaction system that is in a state of equilibrium.

Figure 8.12 Variation of reaction rates and reactant concentrations as equilibrium is established (T_e is the time needed to reach equilibrium).



Instead of writing separate equations for both the forward and reverse reactions, the usual practice is to represent reversibility by double arrows. Thus, the equation for the reaction between H_2 and I_2 is written



8.7 The Position of Equilibrium

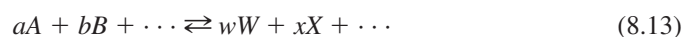
Learning Objective

7. Write equilibrium expressions based on reaction equations, and do calculations based on equilibrium expressions.

position of equilibrium An indication of the relative amounts of reactants and products present at equilibrium.

The **position of equilibrium** for a reaction indicates the relative amounts of reactants and products present at equilibrium. When the position is described as being far to the right, it means that at equilibrium the concentration of products is much higher than the concentration of reactants. A position far to the left means the concentration of reactants is much higher than that of products.

The position of equilibrium can be represented numerically by using the concept of an equilibrium constant. Any reaction that establishes an equilibrium can be represented by a general equation:



In this equation, the capital letters stand for substances such as the H_2 , I_2 , and HI of Equation 8.12, and the lowercase letters are the coefficients in the balanced equation such as the 1, 1, and 2 of Equation 8.12. The dots in Equation 8.13 indicate that any number of reactants and products can be involved in the reaction, but we will limit ourselves to just the four shown.

As we implied earlier, a reaction at equilibrium can be recognized because the concentrations of reactants and products remain constant. That is, they do not change as time passes. For a reaction at equilibrium, the following equation is valid:

$$K = \frac{[W]^w[X]^x}{[A]^a[B]^b} \quad (8.14)$$

equilibrium expression An equation relating the equilibrium constant and reactant and product equilibrium concentrations.

equilibrium constant A numerical relationship between reactant and product concentrations in a reaction at equilibrium.

In this **equilibrium expression**, the brackets $[]$ represent molar concentrations of the reactants (A and B) and the products (W and X). The K is a constant called the **equilibrium constant**, and the powers on each bracket are the coefficients from the balanced equation for the reaction. According to this equation, the product of equilibrium concentrations of products (raised to appropriate powers) divided by the product of the equilibrium concentration of reactants (also raised to appropriate powers) gives a number that does not change with time (the equilibrium constant). The reason K does not change with time is that at equilibrium, the concentrations used to calculate K do not change with time. We could get

a different constant by dividing the reactant concentrations by the product concentrations, but it is the accepted practice to calculate K values as we have shown in Equation 8.14.

Example 8.2

Write equilibrium expressions for the reactions represented by the following equations:

- a. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
- b. $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$

Solution

- a. The concentration of the product HI goes on top and is raised to the power 2. The concentrations of the reactants H_2 and I_2 go on the bottom, and each is raised to the power 1, which is not written but understood:

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

- b. The product is SO_3 , and the power is 2. The reactants are SO_2 (power = 2) and O_2 (power = 1).

$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

Learning Check 8.2

Write equilibrium expressions for the reactions represented by the following equations:

- a. $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$
- b. $3\text{NO}(\text{g}) \rightleftharpoons \text{N}_2\text{O}(\text{g}) + \text{NO}_2(\text{g})$

For a reaction with an equilibrium position far to the right, the product concentrations $[W]$ and $[X]$ will be much higher than the reactant concentrations $[A]$ and $[B]$. According to Equation 8.14, such a situation should result in a large K value. For reactions with equilibrium positions far to the left, a similar line of reasoning leads to the conclusion that K values should be small. Thus, the value of the equilibrium constant gives an indication of the position of equilibrium for a reaction.

Example 8.3

For each of the following equations, the equilibrium molarity concentration is given below each reactant and product. Calculate K for each reaction and comment on the position of equilibrium.

- a. $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$
 $8.23 \times 10^{-3} \text{ M} \qquad 1.46 \times 10^{-2} \text{ M at } 25^\circ\text{C}$
- b. $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$
 $0.200 \text{ M} \qquad 0.150 \text{ M} \qquad 1.37 \times 10^{-2} \text{ M} \qquad 4.11 \times 10^{-2} \text{ M at } 900 \text{ K}$

Solution

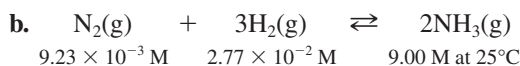
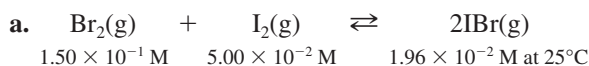
$$\text{a. } K = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{(1.46 \times 10^{-2} \text{ mol/L})}{(8.23 \times 10^{-3} \text{ mol/L})^2} = \frac{2.16 \times 10^2}{\text{mol/L}}$$

We see that K is fairly large, which tells us the equilibrium position is toward the right, or product, side of the reaction. The peculiar sounding “per mole per liter” unit is the result of the way concentration terms are arranged in the equilibrium expression. The unit will not be the same for the K of all reactions. These units are not ordinarily shown, a practice we will follow for the remainder of this chapter.

$$\begin{aligned}
 \text{b. } K &= \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]} \\
 &= \frac{(1.37 \times 10^{-2} \text{ mol/L})(4.11 \times 10^{-2} \text{ mol/L})^3}{(0.200 \text{ mol/L})(0.150 \text{ mol/L})} \\
 &= 3.17 \times 10^{-5}
 \end{aligned}$$

The small value of K indicates the equilibrium position is toward the left.

► **Learning Check 8.3** The molar concentrations are given below the reactants and products in the equations for the following reactions. Calculate K and comment on the position of each equilibrium.



Example 8.3 illustrates that equilibrium constants for different reactions may be small or large. In fact, the two reactions used are by no means even close to the extremes encountered for K values. Some are so small (such as 1.1×10^{-36}) that for all practical purposes no products are present at equilibrium. Others are so large (such as 1.2×10^{40}) that the reaction can be considered to go completely to products. For reactions with K values between 10^{-3} and 10^3 , the position of equilibrium is not extremely favorable to either side, and significant concentrations of both reactants and products can be detected in the equilibrium mixtures.

You might also have noticed in Example 8.3 that the equilibrium concentrations were given for specific temperatures. The reason for this is that K values are constant for a reaction as long as the temperature remains constant. However, K values will change as the temperature is changed. This is a demonstration of the effect of temperature on the position of equilibrium described in the next section.

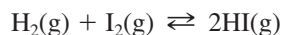
8.8 Factors That Influence Equilibrium Position

Learning Objective

8. Use Le Châtelier's principle to predict the influence of changes in concentration and reaction temperature on the position of equilibrium for reactions.

A number of factors can change the position of an established equilibrium. The influence of such factors can be predicted by using a concept known as Le Châtelier's principle, in honor of its originator. According to **Le Châtelier's principle**, when a change is made in any factor of an established equilibrium, the position of equilibrium will shift in a direction that will minimize or oppose the change. The factors we will be most concerned with are concentrations of reactants and products, and reaction temperature.

The effect of concentration changes can be illustrated by the reaction of H_2 with I_2 (Equation 8.12):



Suppose an equilibrium mixture of H_2 , I_2 , and HI is formed. According to the molecular collision concept, favorable collisions are occurring between H_2 and I_2 molecules to form HI molecules, and favorable collisions are also taking place between HI molecules that cause them to form H_2 and I_2 molecules. Now, suppose some additional I_2 is added to the equilibrium mixture. The chances for favorable collisions between H_2 and I_2 molecules are increased; the rate of formation of HI is increased, and more HI is formed than disappears. The rate of reaction of HI to give H_2 and I_2 increases as the concentration of HI increases,

Le Châtelier's principle The position of an equilibrium shifts in response to changes made in factors of the equilibrium.

The True Value of Platinum and Gold



Metallic gold has been known since prehistoric times and used through much of human history. This is likely the result of the resistance of gold to react with other materials and undergo such processes as corrosion. This property also explains why gold occurs in nature primarily in the form of small metallic grains or nuggets, or as veins of the metal in rocks. Skillfully worked gold jewelry has been found in good condition in royal graves known to be at least 5000 years old.

Historically, gold has been regarded as the ultimate symbol of political power and wealth. The mythical king Midas could turn any material into gold simply by touching it. The biblical king Solomon built a temple and had all the inside surfaces overlaid with gold. Today, the highest achievements in athletics and other competitions are often recognized by the awarding of gold medals.

Does gold live up to this symbolic reputation in terms of its actual price when bought and sold in the marketplace? In the past, its market value remained quite high compared to other precious metals such as silver and platinum. However, by the year 2000 the price of platinum had increased more rapidly than gold and they both sold for about \$400 per ounce. The price of platinum continued to increase more rapidly than gold and by 2005, platinum sold for \$850 per ounce compared to gold's price of \$425 per ounce.

The value of platinum overtaking the value of gold is a classic case of economics and the concept of supply and demand. During each of the years between 2000 and 2005, worldwide demand for platinum exceeded the supply. As a result, the market price of platinum increased. But why did the demand for platinum increase at a greater rate than the demand for gold? The answer becomes evident when the pattern of use for each metal is analyzed.

About 75% of the gold produced worldwide is used to make jewelry. Much smaller amounts are used in other ways such as dental work, electronic devices and glass making. In dental work, alloys of gold are used to make crowns, fillings and bridges. The electronics industry uses electroplated gold to prevent corrosion of electrical connections, printed circuit boards and other copper components. Colloidal gold

added to molten glass gives the finished glass a red-to-purple color, and metallic gold applied as a thin film to window glass reflects heat from sunlight that falls on the windows.

Like gold, the largest use of platinum is for jewelry making, but this accounts for only 50% of the worldwide production. Another 30% is used to make catalytic converters for the exhaust system of automobiles, and the remaining 20% goes into other industrial applications. It has been estimated that one of every five purchased products contains some platinum or requires platinum for its production.

Most of the non-jewelry applications of platinum utilize its ability to act as a catalyst in chemical reactions. Catalytic converters are devices attached to the end of the exhaust system of internal combustion engines. At the high temperature of combustion in these engines, hydrocarbon-containing fuels such as gasoline are mixed with air (O_2 and N_2 gases) and, ideally, burned to form carbon dioxide gas (CO_2) and water vapor (H_2O). However, the ideal reactions do not take place completely during combustion, and small amounts of undesirable products are also formed, including carbon monoxide (CO) and nitrogen oxide (NO). These undesirable products and a small amount of unburned fuel are then included in the exhaust given off by the engine. When they are exposed to sunlight, these unhealthy air pollutants are converted into an unhealthy mixture of other substances called smog. The role of the catalytic converter is to catalyze the conversion of the CO , NO and unburned hydrocarbons into CO_2 , H_2O and nitrogen gas, N_2 . The use of catalytic converters on exhaust systems has had a significant impact on air quality in the cities of the world. In 1960, the exhaust from an average automobile contained 100 grams of pollutants for each mile driven. A modern automobile equipped with a catalytic converter puts out only about 2 grams of pollutants per mile. The catalytic property of platinum is also employed in numerous industrial processes such as the production of nitric acid, a very important industrial chemical.

The use of platinum and gold as components of jewelry or other decorative objects has changed little during the last 50 years. However, the increased industrial use of platinum as a catalyst during that time is the factor that accounts for its increased demand and accompanying price increase. Thus, the true value of gold or platinum, as measured by importance to society, is not so much in their use to adorn ourselves and impress others, but more in how they are used in practical, beneficial ways.



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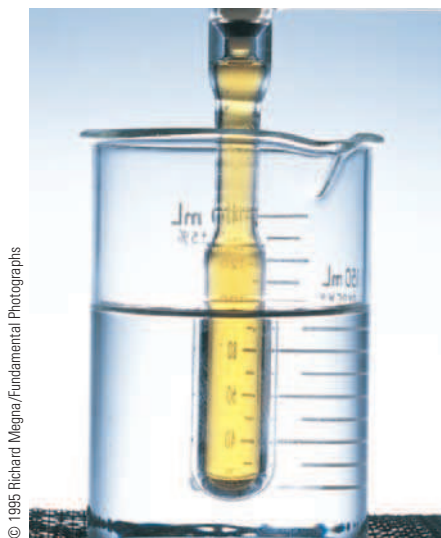
The production of jewelry accounts for the largest use of gold in the world today.



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Platinum metal in the form of a woven fabric functions as a catalyst in this industrial equipment.

Figure 8.13 The effect of temperature on the position of equilibrium for the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$. On which side of the equation will heat appear? Is the reaction exothermic or endothermic?



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- 1 A sealed tube containing an equilibrium mixture of red-brown NO_2 and colorless N_2O_4 is cooled in an ice bath.



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- 2 The same sealed tube is heated in a hot water bath.

and eventually a new equilibrium position and a new set of equilibrium concentrations will be established. The new equilibrium mixture will contain more HI than the original mixture, but the amounts of the reactants will also be different such that the equilibrium constant remains unchanged. The original equilibrium of the reaction has been shifted toward the right.

Le Châtelier's principle can also be used to predict the influence of temperature on an equilibrium by treating heat as a product or reactant. Consider the following equation for a hypothetical exothermic reaction:



If the temperature is increased (by adding more heat, which appears on the right side of the equation), the equilibrium shifts to the left in an attempt to use up the added heat. In the new equilibrium position, the concentrations of A and B will be higher, whereas the chemical product concentrations will be lower than those in the original equilibrium. In this case the value of the equilibrium constant is changed by the change in temperature (see Figure 8.13).

Example 8.4

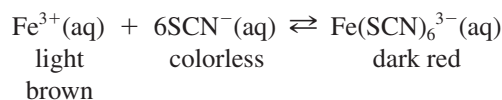
Using Le Châtelier's principle, answer the following questions:

- a. Ammonia is made from hydrogen and atmospheric nitrogen:



What effect will cooling have on an equilibrium mixture?

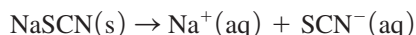
- b. What effect will removing H_2 have on the equilibrium mixture described in part a?
c. Consider the following equation for a reaction that takes place in solution:



What effect will the addition of colorless NaSCN solid have on the color of the solution?

Solution

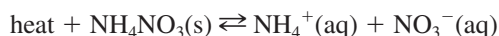
- Heat is removed by cooling. Heat is replenished when the equilibrium shifts to the right. Thus, more NH_3 will be present at equilibrium in the cooler mixture.
- The equilibrium will shift to the left in an attempt to replenish the H_2 . At the new equilibrium position, less NH_3 will be present.
- When solid NaSCN is added, it will dissolve and form ions:



The SCN^- concentration in the solution will therefore be increased. In an attempt to use up the added SCN^- , the equilibrium will shift to the right. This shift generates more of the dark red Fe(SCN)_6^{3-} . Therefore, the new position of equilibrium will be characterized by a darker red color.

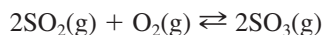
Learning Check 8.4 Use Le Châtelier's principle and answer the following:

- A saturated solution of ammonium nitrate is formed as follows. The solution process is endothermic:



Which way will the equilibrium shift when heat is added? What does this shift mean in terms of the solubility of NH_4NO_3 at the higher temperature?

- Sulfur trioxide gas is formed when oxygen and sulfur dioxide gas react:



Which way would the equilibrium shift if O_2 were removed from the system? How would the new equilibrium concentration of SO_3 compare with the earlier equilibrium concentration?

Catalysts cannot change the position of an equilibrium. This fact becomes clear when you remember that a catalyst functions by lowering the activation energy for a reaction. A lowering of the energy barrier for the forward reaction also lowers the barrier for the reverse reaction (see Figure 8.14). Hence, a catalyst speeds up both the forward and reverse reactions and cannot change the position of equilibrium. However, the lowered activation energy allows equilibrium to be established more quickly than if the catalyst were absent.

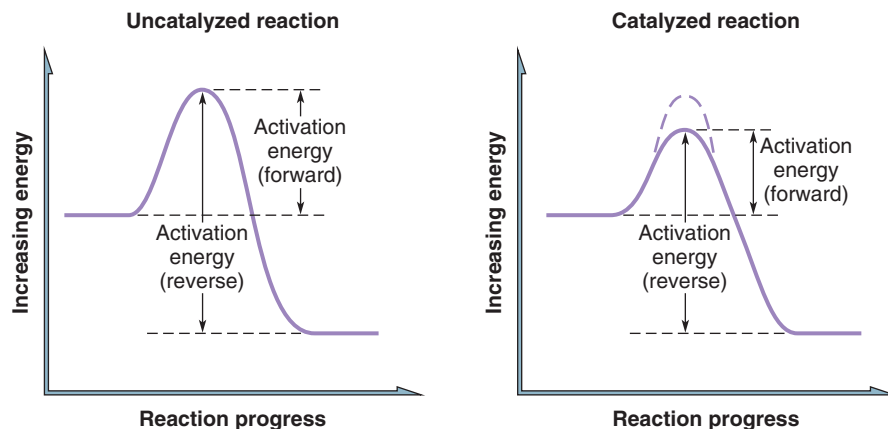


Figure 8.14 The influence of catalysts on forward and reverse activation energies.

Study Skills 8.1 Le Châtelier's Principle in Everyday Life

Le Châtelier's principle is extremely important in laboratory work and in the chemical industry when the goal is to obtain the maximum amount of product from a reaction. In such cases, increasing reactant concentrations, or adjusting the reaction temperature or pressure to shift the equilibrium position to the product side of the reaction, is a common practice.

To help you understand Le Châtelier's principle, it is often useful to observe familiar situations and events and interpret them in terms of shifting equilibria. For example, when you stand in an upright position, you are in equilibrium with the force of gravity. If a friend leans against you, your equilibrium is upset, and you will lose your balance unless you respond by leaning toward your friend such that the forces on you are once again balanced.

Children playing on a seesaw provide a similar example of forces in equilibrium. If one child slides toward the center of the

seesaw, the force acting on that side is reduced, the equilibrium is upset, and the other child will be firmly on the ground. However, if the second child also shifts toward the center, the forces on each side can be made equal again, and play can resume.

The preceding examples involved equilibrium between forces, but we are not limited to only those types of examples. Imagine you are enjoying a warm shower when someone turns on a nearby hot water faucet. Suddenly, your shower turns cold. You respond to this stress by adjusting the shower controls (after shrieking loudly) to let in more hot water in an attempt to restore the pleasant temperature you were enjoying. (However, be aware of what will happen when the other faucet is turned off.)

Be mindful of your surroundings and activities, and you will see many more examples that will remind you of responses to stress that are attempts to restore equilibrium to a previous situation.

Concept Summary

Spontaneous and Nonspontaneous Processes. Spontaneous processes take place naturally with no apparent cause or stimulus. Process spontaneity depends on the energy and entropy changes that accompany the process. Energy decreases and entropy increases favor spontaneity. However, a nonspontaneous change in one of these factors can be compensated for by a large spontaneous change in the other to cause processes to be spontaneous.

Objective 1, Exercise 8.6

Reaction Rates. The speed of a reaction is called a reaction rate, which can be determined by measuring how fast reactants are used up or products are formed.

Objective 2, Exercise 8.14

Molecular Collisions. Explanations of how reactions take place are called reaction mechanisms. Most mechanisms are based on three assumptions: (1) Molecules must collide with one another, (2) the collision must involve a certain minimum of energy, and (3) some colliding molecules must be oriented in a specific way during collision in order to react.

Objective 3, Exercise 8.20

Energy Diagrams. Energy relationships for reactions can be represented by energy diagrams, in which energy is plotted versus the reaction progress. The concepts of exothermic and endothermic reactions and activation energy are clearly represented by such diagrams.

Objective 4, Exercise 8.26

Factors That Influence Reaction Rates. Four factors affect the rates of all reactions: (1) the nature of the reactants, (2) reactant concentrations, (3) reactant temperature, and (4) the presence of catalysts.

Objective 5, Exercise 8.30

Chemical Equilibrium. Reactions are in equilibrium when the rate of the forward reaction is equal to the rate of the reverse reaction. Equilibrium is emphasized in equations for reactions by writing double arrows pointing in both directions between reactants and products.

Objective 6, Exercise 8.38

The Position of Equilibrium. The relative amounts of reactants and products present in a system at equilibrium define the position of equilibrium. The equilibrium position is toward the right when a large amount of product is present and toward the left when a large amount of reactant is present. The position is indicated by the value of the equilibrium constant.

Objective 7, Exercises 8.40 and 8.46

Factors That Influence Equilibrium Position. Factors known to influence the position of equilibrium include changes in amount of reactants and/or products and changes in temperature. The influence of such factors can be predicted by using Le Châtelier's principle. Catalysts cannot change the position of equilibrium.

Objective 8, Exercise 8.52

Key Terms and Concepts

Activation energy (8.3)

Catalyst (8.5)

Effective collision (8.5)

Endergonic process (8.1)

Entropy (8.1)

Equilibrium concentrations (8.6)

Equilibrium constant (8.7)

Equilibrium expression (8.7)

Exergonic process (8.1)

Heterogeneous (surface) catalyst (8.5)

Homogeneous catalyst (8.5)

Inhibitor (8.5)

Internal energy (8.3)

Le Châtelier's principle (8.8)

Position of equilibrium (8.7)

Reaction mechanism (8.3)

Reaction rate (8.2)

Spontaneous process (8.1)

Stable substance (8.1)

State of equilibrium (8.6)

Key Equations

1. Calculation of reaction rate (Section 8.2): $\text{Rate} = \frac{\Delta C}{\Delta t} = \frac{C_t - C_0}{\Delta t}$ Equation 8.1

2. Equilibrium expression for general reaction (Section 8.7): $aA + bB + \cdots \rightleftharpoons wW + xX + \cdots$ Equation 8.13

$$K = \frac{[W]^w[X]^x}{[A]^a[B]^b}$$
 Equation 8.14

Exercises

 **OWL** Interactive versions of these problems are assignable in OWL.

Even-numbered exercises are answered in Appendix B.

Blue-numbered exercises are more challenging.

Spontaneous and Nonspontaneous Processes (Section 8.1)

- 8.1** Classify the following processes as spontaneous or nonspontaneous. Explain your answers in terms of whether energy must be continually supplied to keep the process going.
- Water is decomposed into hydrogen and oxygen gas by passing electricity through the liquid.
 - An explosive detonates after being struck by a falling rock.
 - A coating of magnesium oxide forms on a clean piece of magnesium exposed to air.
 - A light bulb emits light when an electric current is passed through it.
 - A cube of sugar dissolves in a cup of hot coffee.
- 8.2** Classify the following processes as spontaneous or nonspontaneous. Explain your answers in terms of whether energy must be continually supplied to keep the process going.
- The space shuttle leaves its pad and goes into orbit.
 - The fuel in a booster rocket of the space shuttle burns.
 - Water boils at 100°C and 1 atm pressure.
 - Water temperature increases to 100°C at 1 atm pressure.
 - Your bedroom becomes orderly.
- 8.3** Classify the following processes as exergonic or endergonic. Explain your answers.
- Any combustion process
 - Perspiration evaporating from the skin
 - Melted lead solidifying
 - An explosive detonating
 - An automobile being pushed up a slight hill (from point of view of the automobile)
- 8.4** Classify the following processes as exergonic or endergonic. Explain your answers.
- An automobile being pushed up a slight hill (from point of view of the one pushing)
 - Ice melting (from point of view of the ice)
 - Ice melting (from point of view of surroundings of the ice)
 - Steam condensing to liquid water (from point of view of the steam)
 - Steam condensing to liquid water (from point of view of surroundings of the steam)
- 8.5** Describe the energy and entropy changes that occur in the following processes, and indicate whether the processes are spontaneous under the conditions stated:
- Lumber becomes a house
 - A seed grows into a tree
 - On a hot day, water evaporates from a lake
- 8.6** Describe the energy and entropy changes that occur in the following processes, and indicate whether the processes are spontaneous under the conditions stated:
- On a cold day, water freezes.
 - A container of water at 40°C cools to room temperature.
 - The odor from an open bottle of perfume spreads throughout a room.
- 8.7** Pick the example with the highest entropy from each of the following sets. Explain your answers.
- Solid ice, liquid water, or steam
 - Leaves on a tree, fallen leaves blown about on the ground, fallen leaves raked and placed in a basket
 - A stack of sheets of paper, a wastebasket containing sheets of paper, a wastebasket containing torn and crumpled sheets of paper
 - A 0.10 M sugar solution, a 1.0 M sugar solution, a 10.0 M sugar solution
 - A banquet table set for dinner, a banquet table during dinner, a banquet table immediately after dinner
- 8.8** Pick the example with the highest entropy from each of the following sets. Explain your answers.
- Two opposing football teams just before the ball is snapped, two opposing football teams 1 second after the ball is snapped, two opposing football teams when the whistle is blown, ending the play
 - A 10% copper/gold alloy, a 2% copper/gold alloy, pure gold
 - A purse on which the strap just broke, a purse just hitting the ground, a purse on the ground with contents scattered
 - Coins in a piggy bank, coins in piles containing the same type of coins, coins in stacks of the same type of coins
 - A dozen loose pearls in a box, a dozen pearls randomly strung on a string, a dozen pearls strung on a string in order of decreasing size

- 8.9** You probably know that, on exposure to air, silver tarnishes and iron rusts; but gold, stainless steel, and chromium do not change. Explain these facts, using the concept of stability.

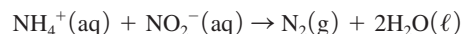
Reaction Rates (Section 8.2)

- 8.10** Classify the following processes according to their rates as very slow, slow, or fast:
- The souring of milk stored in a refrigerator
 - The cooking of an egg in boiling water
 - The ripening of a banana stored at room temperature
 - The rising of bread dough in a warm room
 - The melting of butter put into a hot pan
- 8.11** Classify the following processes according to their rates as very slow, slow, or fast:
- The change of apple juice to cider
 - The movement of sound from a slammed door to your ear
 - The ringing of your phone after you step into the shower
 - The combustion of gasoline in the engine of your car
 - The perceived passage of time when you are doing something enjoyable
- 8.12** Describe the observations or measurements that could be made to allow you to follow the rate of the following processes:
- The melting of a block of ice
 - The setting (hardening) of concrete
 - The burning of a candle
- 8.13** Describe the observations or measurements that could be made to allow you to follow the rate of the following processes:
- The diffusion of ink from a drop placed in a pan of quiet, undisturbed water
 - The loss of water from a pan of boiling water
 - The growth of a corn plant
- 8.14** Consider the following hypothetical reaction:
- $$A + B \rightarrow C$$
- Calculate the average rate of the reaction on the basis of the following information:
- Pure *A* and *B* are mixed, and after 12.0 minutes the measured concentration of *C* is 0.396 mol/L.
 - Pure *A*, *B*, and *C* are mixed together at equal concentrations of 0.300 M. After 8.00 minutes, the concentration of *C* is found to be 0.455 M.
- 8.15** Consider the following reaction:
- $$A + B \rightarrow C$$
- Calculate the average rate of the reaction on the basis of the following information:
- Pure *A*, *B*, and *C* are mixed together at concentrations of $A = B = 0.400$ M, $C = 0.150$ M. After 6.00 minutes, the concentration of *C* is 0.418 M.
 - Pure *A* and *B* are mixed together at the same concentration of 0.361 M. After 7.00 minutes, the concentration of *A* is found to be 0.048 M.

- 8.16** A reaction generates carbon dioxide gas (CO_2) as a product. The reactants are mixed in a sealed 500-mL vessel. After 25.0 minutes, 1.93×10^{-3} mol CO_2 has been generated. Calculate the average rate of the reaction.

- 8.17** A reaction generates hydrogen gas (H_2) as a product. The reactants are mixed in a sealed 250-mL vessel. After 20.0 minutes, 3.91×10^{-2} mol H_2 has been generated. Calculate the average rate of the reaction.

- 8.18** Ammonium and nitrite ions react in solution to form nitrogen gas:



A reaction is run, and the liberated N_2 gas is collected in a previously evacuated 500-mL container. After the reaction has gone on for 750 seconds, the pressure of N_2 in the 500-mL container is 2.77×10^{-2} atm, and the temperature of the N_2 is 25.0°C . Use the ideal gas law (Equation 6.9) to calculate the number of moles of N_2 liberated. Then calculate the average rate of the reaction.

- 8.19** Suppose a small lake is contaminated with an insecticide that decomposes with time. An analysis done in June shows the decomposition product concentration to be 7.8×10^{-4} mol/L. An analysis done 35 days later shows the concentration of decomposition product to be 9.9×10^{-4} mol/L. Assume the lake volume remains constant and calculate the average rate of decomposition of the insecticide.

Molecular Collisions (Section 8.3)

- 8.20** In each of the following, which reaction mechanism assumption is apparently being violated? Explain your answers.
- A reaction takes place more rapidly when the concentration of reactants is decreased.
 - A reaction takes place more rapidly when the reaction mixture is cooled.
 - The reaction rate of $A + B \rightarrow A-B$ increases as the concentration of *A* is increased but does not change as the concentration of *B* is increased.
- 8.21** Which reaction mechanism assumptions are unimportant in describing simple ionic reactions between cations and anions? Why?
- 8.22** Describe two ways by which an increase in temperature increases a reaction rate.

Energy Diagrams (Section 8.4)

- 8.23** Sketch energy diagrams to represent each of the following. Label the diagrams completely and tell how they are similar to each other and how they are different.
- Exothermic (exergonic) reaction with activation energy
 - Exothermic (exergonic) reaction without activation energy
- 8.24** Sketch energy diagrams to represent each of the following. Label the diagrams completely and tell how they are similar to each other and how they are different.
- Endothermic (endergonic) reaction with activation energy
 - Endothermic (endergonic) reaction without activation energy
- 8.25** Use energy diagrams to compare catalyzed and uncatalyzed reactions.

- 8.26** One reaction occurs at room temperature and liberates 500 kJ/mol of reactant. Another reaction does not take place until the reaction mixture is heated to 150°C. However, it also liberates 500 kJ/mol of reactant. Draw an energy diagram for each reaction and indicate the similarities and differences between the two.

Factors That Influence Reaction Rates (Section 8.5)

- 8.27** The following reactions are proposed. Make a rough estimate of the rate of each one—rapid, slow, won't react. Explain each answer.
- $\text{H}_2\text{O}(\ell) + \text{H}^+(\text{aq}) \rightarrow \text{H}_3\text{O}^+(\text{aq})$
 - $\text{H}_3\text{O}^+(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_4\text{O}^{2+}(\text{aq})$
 - $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
 - $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$
- 8.28** The following reactions are proposed. Make a rough estimate of the rate of each one—rapid, slow, won't react. Explain each answer.
- $\text{CaO}(\text{s}) + 2\text{HCl}(\text{g}) \rightarrow \text{CaCl}_2(\text{s}) + \text{H}_2\text{O}(\ell)$
 - $2\text{KI}(\text{s}) + \text{Pb}(\text{NO}_3)_2(\text{s}) \rightarrow \text{PbI}_2(\text{s}) + 2\text{KNO}_3(\text{s})$
 - $\text{Cl}^-(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{ICl}_2^-(\text{aq})$
 - $\text{I}_2(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{I}_3^-(\text{aq})$
- 8.29** Which reaction mechanism assumption is most important in explaining the following? Why?
- The influence of concentration on reaction rates
 - The influence of catalysts on reaction rates
- 8.30** Suppose you are running a reaction and you want to speed it up. Describe three things you might try to do this.
- 8.31** A reaction is started by mixing reactants. As time passes, the rate decreases. Explain this behavior that is characteristic of most reactions.
- 8.32** A reaction is run at 10°C and takes 3.7 hours to go to completion. How long would it take to complete the reaction at 30°C?
- 8.33** What factor is more important than simply the amount of solid reactant present in determining the rate of a reaction? Explain.
- 8.34** Describe two ways catalysts might speed up a reaction.

Chemical Equilibrium (Section 8.6)

- 8.35** Describe the establishment of equilibrium in a system represented by a shopper walking up the “down” escalator.
- 8.36** Describe the observation or measurement result that would indicate when each of the following had reached equilibrium:
- $$\begin{array}{ccccc} \text{H}_2 & + & \text{I}_2 & \rightleftharpoons & 2\text{HI} \\ \text{colorless gas} & & \text{violet gas} & & \text{colorless gas} \end{array}$$
 - solid sugar + water \rightleftharpoons sugar solution
 - $$\begin{array}{ccccc} \text{N}_2 & + & 2\text{O}_2 & \rightleftharpoons & 2\text{NO}_2 \\ \text{colorless gas} & & \text{colorless gas} & & \text{red-brown gas} \end{array}$$
- 8.37** Describe the observation or measurement result that would indicate when each of the following had reached equilibrium:
- $$\begin{array}{ccccc} 2\text{CO} & + & \text{O}_2 & \rightleftharpoons & 2\text{CO}_2 \\ \text{colorless gas} & & \text{colorless gas} & & \text{colorless gas} \end{array}$$

(apply Dalton's law)

- $$\begin{array}{ccccc} \text{LiOH} & + & \text{CO}_2 & \rightleftharpoons & \text{LiHCO}_3 \\ \text{colorless solid} & & \text{colorless gas} & & \text{colorless solid} \end{array}$$
- paycheck \rightarrow checking account \rightarrow checks to pay bills

- 8.38** Colorless hydrogen gas (H_2) and red-brown colored bromine gas (Br_2) react to form colorless HBr gas. Describe how the concentrations of H_2 , Br_2 , and HBr would change (increase or decrease) as equilibrium was established in a sealed container that initially contained only H_2 and Br_2 . What observation would indicate that equilibrium had been established?
- 8.39** Colorless N_2O_4 gas decomposes to form red-brown colored NO_2 gas. Describe how the concentrations of N_2O_4 and NO_2 would change (increase or decrease) as equilibrium was established in a sealed container that was initially filled with N_2O_4 . What observation would indicate that equilibrium had been established?

The Position of Equilibrium (Section 8.7)

- 8.40** Write an equilibrium expression for each of the following gaseous reactions:
- $\text{CH}_4 + 2\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O}$
 - $2\text{O}_3 \rightleftharpoons 3\text{O}_2$
 - $\text{H}_2 + \text{CO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO}$
 - $4\text{NH}_3 + 7\text{O}_2 \rightleftharpoons 4\text{NO}_2 + 6\text{H}_2\text{O}$
 - $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$
- 8.41** Write an equilibrium expression for each of the following gaseous reactions:
- $\text{H}_2 + \text{Br}_2 \rightleftharpoons 2\text{HBr}$
 - $2\text{H}_2\text{S} + 3\text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + 2\text{SO}_2$
 - $3\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5 + \text{NO}$
 - $4\text{NH}_3 + 3\text{O}_2 \rightleftharpoons 2\text{N}_2 + 6\text{H}_2\text{O}$
 - $2\text{NO} + 2\text{H}_2 \rightleftharpoons \text{N}_2 + 2\text{H}_2\text{O}$
- 8.42** The following equilibria are established in water solutions. Write an equilibrium expression for each reaction.
- $\text{Au}^+ + 2\text{CN}^- \rightleftharpoons \text{Au}(\text{CN})_2^-$
 - $\text{Pt}^{2+} + 4\text{Cl}^- \rightleftharpoons \text{PtCl}_4^{2-}$
 - $\text{Co}^{2+} + 6\text{NH}_3 \rightleftharpoons \text{Co}(\text{NH}_3)_6^{2+}$
- 8.43** The following equilibria are established in water solutions. Write an equilibrium expression for each reaction.
- $\text{Ni}^{2+} + 6\text{NH}_3 \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}$
 - $\text{Sn}^{2+} + 2\text{Fe}^{3+} \rightleftharpoons \text{Sn}^{4+} + 2\text{Fe}^{2+}$
 - $\text{F}_2 + 2\text{Cl}^- \rightleftharpoons 2\text{F}^- + \text{Cl}_2$
- 8.44** Write an equation that corresponds to each of the following equilibrium expressions:
- $K = \frac{[\text{CO}_2]^2}{[\text{CO}]^2[\text{O}_2]}$
 - $K = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]}$
 - $K = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{O}_2]}$
 - $K = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$

- 8.56** Tell what will happen to each equilibrium concentration in the following when the indicated stress is applied and a new equilibrium position is established:
- $\text{LiOH(s)} + \text{CO}_2\text{(g)} \rightleftharpoons \text{LiHCO}_3\text{(s)} + \text{heat}$; CO_2 is removed.
 - $2\text{NaHCO}_3\text{(s)} + \text{heat} \rightleftharpoons \text{Na}_2\text{O(s)} + 2\text{CO}_2\text{(g)} + \text{H}_2\text{O(g)}$; the system is cooled.
 - $\text{CaCO}_3\text{(s)} + \text{heat} \rightleftharpoons \text{CaO(s)} + \text{CO}_2\text{(g)}$; the system is cooled.
- 8.57** The gaseous reaction $2\text{HBr(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{Br}_2\text{(g)}$ is endothermic. Tell which direction the equilibrium will shift for each of the following:
- Some H_2 is removed.
 - The temperature is decreased.
 - Some Br_2 is added.
 - A catalyst is added.
 - Some HBr is added.
 - The temperature is decreased, and some HBr is removed.
- 8.58** The gaseous reaction $\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{NO(g)}$ is exothermic. Tell which direction the equilibrium will shift for each of the following:
- Some N_2 is removed.
 - The temperature is decreased.
 - Some NO is added.
 - Some O_2 is removed.
 - A catalyst is added.
 - The temperature is increased, and some O_2 is removed.

Additional Exercises

- 8.59** Assume the following reactions take place under identical conditions of concentration and temperature. Which reaction would you expect to take place faster? Explain your answer.
- $\text{H}_2\text{(g)} + \text{F}_2\text{(g)} \rightarrow 2\text{HF(g)}$
 - $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightarrow 2\text{HI(g)}$
- 8.60** Gases A and B react as follows: $A\text{(g)} + B\text{(g)} \rightarrow C\text{(s)}$. Suppose gases A and B are mixed and used to fill a balloon. How could you increase the concentration of A and B , and speed up the reaction?
- 8.61** Bacteria found in lakes use dissolved oxygen gas to metabolize organic contaminants and use them as a food source, thus removing the contaminants from the lakes. When lake temperatures increase significantly, the rate of this chemical decontamination decreases. Remember your study of gases and explain this apparent violation of the factors influencing reaction rates studied in this chapter.
- 8.62** In Section 8.1 of this chapter, three criteria that determine the spontaneity of a process are given. Review these criteria, and determine which one is involved in each of the following spontaneous phase changes:
- Evaporation of a liquid
 - Condensation of a gas to a liquid
 - Sublimation of a solid to a gas
 - Liquefaction of a gas to a liquid
 - Crystallization of a liquid to a solid

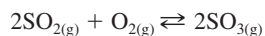
Allied Health Exam Connection

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- 8.63** A reaction takes place between an acid and 0.5 grams of solid magnesium ribbon. Another reaction takes place between an acid and 0.5 grams of powdered magnesium. Which statement is true?
- The powdered magnesium reacts faster because the activation energy has been lowered.
 - The magnesium strip reacts faster because it has a higher concentration of magnesium.
 - The powdered magnesium reacts faster because it has a greater surface area.
 - The magnesium strip reacts faster because it will create a higher temperature once the reaction starts.
- 8.64** If the reaction: $A + B \rightarrow C + D$ is designated as first order, the rate depends on:
- the concentration of only one reactant
 - the concentration of each reactant
 - no specific concentration
 - the temperature only
- 8.65** Reaction kinetics deals with:
- equilibrium position
 - reaction rates
 - molecular reactant size
 - none of the above
- 8.66** A book is held six feet above the floor and then dropped. Which statement is true?
- The potential energy of the book is converted to kinetic energy.
 - The potential energy of the book is destroyed.
 - Kinetic energy is created.
 - The total energy of the system will not be conserved.
- 8.67** When a crane at a building site lifts a beam to its top height, what type of energy is created?
- kinetic energy
 - potential energy
 - chemical energy
 - electrical energy

- 8.68** Stored energy is referred to as:
- activation energy
 - kinetic energy
 - potential energy
 - electrical energy
- 8.69** In exergonic reactions, the energy is:
- used
 - stored
 - released
 - lost
- 8.70** Which is an example of an exothermic change?
- sublimation
 - condensation
 - melting
 - evaporation
- 8.71** Which of the following reactions releases heat energy?
- double replacement
 - decomposition
 - endothermic
 - exothermic
- 8.72** Which of the following is the best example of potential energy changing to kinetic energy?
- Pushing a rock off a cliff
 - Sitting in a rocking chair
 - Observing a bird fly
 - Standing on a table
- 8.73** Which is NOT an example of an endothermic change?
- melting
 - sublimation
 - freezing
 - evaporation
- 8.74** Which of the following processes is endothermic?
- ice melting
 - a piece of paper burning
 - a bomb exploding
 - an organism's metabolism producing a certain amount of heat
- 8.75** Which sentence best describes the following reaction?
- $$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\ell) + \text{heat}$$
- It is an endothermic reaction.
 - It is an exothermic double replacement reaction.
 - It is a synthesis reaction that is also exothermic.
 - It is a decomposition reaction that is also endothermic.
- 8.76** By which of the following mechanisms does a catalyst operate?
- It decreases the activation energy barrier for a reaction.
 - It serves as a reactant and is consumed.
 - It increases the temperature of a reaction.
 - It increases the concentration of reactants.
- 8.77** Which of the following is NOT true of reversible chemical reactions?
- A chemical reaction is never complete.
 - The products of the reaction also react to reform the original reactants.
 - When the reaction is finished, both reactants and products are present in equal amounts.
 - The reaction can result in an equilibrium.
- 8.78** Given the reaction:
- $$2\text{CO}(\text{g}) + \text{O}_2(\text{g}) = 2\text{CO}_2(\text{g})$$
- When there is an increase in pressure to the system one would expect:
- an increase in the amount of carbon dioxide
 - an increase in the amount of carbon monoxide and oxygen
 - a decrease in the amount of carbon dioxide
 - no change in the system
- 8.79** The following reaction is exothermic: $\text{AgNO}_3 + \text{NaCl} \leftrightarrow \text{AgCl} + \text{NaNO}_3$. How will the equilibrium be changed if the temperature is increased?
- Equilibrium will shift to the right.
 - Equilibrium will shift to the left.
 - The reaction will not proceed.
 - Equilibrium will not change.
- 8.80** Consider the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g}) + \text{heat}$. Indicate the incorrect statement.
- An increase in temperature will shift the equilibrium to the right.
 - An increase in pressure applied will shift the equilibrium to the right.
 - The addition of ammonia will shift the equilibrium to the left.
 - The addition of H_2 will shift the equilibrium to the right.
- 8.81** In a chemical reaction, [A] and [B] combine to form [C] and [D], as expressed by the reaction $[\text{A}] + [\text{B}] = [\text{C}] + [\text{D}]$. Select the statement that best describes the equilibrium condition.
- The reaction is shifted to the right.
 - The concentrations of reactants and products are constant.
 - The reaction is shifted to the left.
 - The concentration of products is greater than the concentration of reactants.
- 8.82** What is the effect of the addition of a catalyst to a reaction in equilibrium?
- The reaction favors the formation of the products.
 - The reaction favors the formation of the reactants.
 - There is no change in composition of the reaction.
 - The rate of the reaction slows.
- 8.83** For the reaction: $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$, the reaction can be driven to the left by:
- increasing the pressure
 - increasing the hydrogen
 - increasing hydrogen bromide
 - decreasing hydrogen bromide

8.84 What is the equilibrium constant K_c for the following equation?



- a. $K_c = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]}$
b. $K_c = \frac{[\text{SO}_2][\text{O}_2]}{[\text{SO}_3]}$
c. $K_c = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2}$
d. $K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$

Chemistry for Thought

8.85 Refer to Figure 8.4 and answer the question. How would the total energy released as light for each light stick compare when they have both stopped glowing?

8.86 A mixture of the gases NOCl , NO , and Cl_2 is allowed to come to equilibrium at 400°C in a 1.50-L reaction container. Analysis shows the following number of moles of each substance to be present at equilibrium: $\text{NOCl} = 1.80$ mol, $\text{NO} = 0.70$ mol, and $\text{Cl}_2 = 0.35$ mol. Calculate the value of the equilibrium constant for the reaction at 400°C . The equation for the reaction is



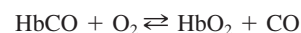
8.87 The equilibrium constant for the reaction $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$ is 0.0245 at 250°C . What molar concentration of PCl_5 would be present at equilibrium if the concentrations of PCl_3 and Cl_2 were both 0.250 M?

8.88 At 448°C , the equilibrium constant for the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ is 50.5. What concentration of I_2 would be found in an equilibrium mixture in which the concentrations of HI and H_2 were 0.500 M and 0.050 M, respectively?

8.89 Refer to Figure 8.10 and answer the questions. Would you expect a crushed antacid tablet (like Alka-Seltzer) to dissolve faster or slower than a whole tablet? Explain.

8.90 Refer to Figure 8.13 and answer the questions. Would the presence of a catalyst in the tube influence the equilibrium concentrations of the two gases? Explain.

8.91 In the blood, both oxygen (O_2) and poisonous carbon monoxide (CO) can react with hemoglobin (Hb). The respective compounds are HbO_2 and HbCO . When both gases are present in the blood, the following equilibrium is established.



Use Le Châtelier's principle to explain why pure oxygen is often administered to victims of CO poisoning.

8.92 Use the concept of reaction rates to explain why no smoking is allowed in hospital areas where patients are being administered oxygen gas.

8.93 Suppose you have two identical unopened bottles of carbonated beverage. The contents of both bottles appear to be perfectly clear. You loosen the cap of one of the bottles and hear a hiss as gas escapes, and at the same time gas bubbles appear in the liquid. The liquid in the unopened bottle still appears to be perfectly clear. Explain these observations using the concept of equilibrium and Le Châtelier's principle. Remember, a carbonated beverage contains carbon dioxide gas dissolved in a liquid under pressure.

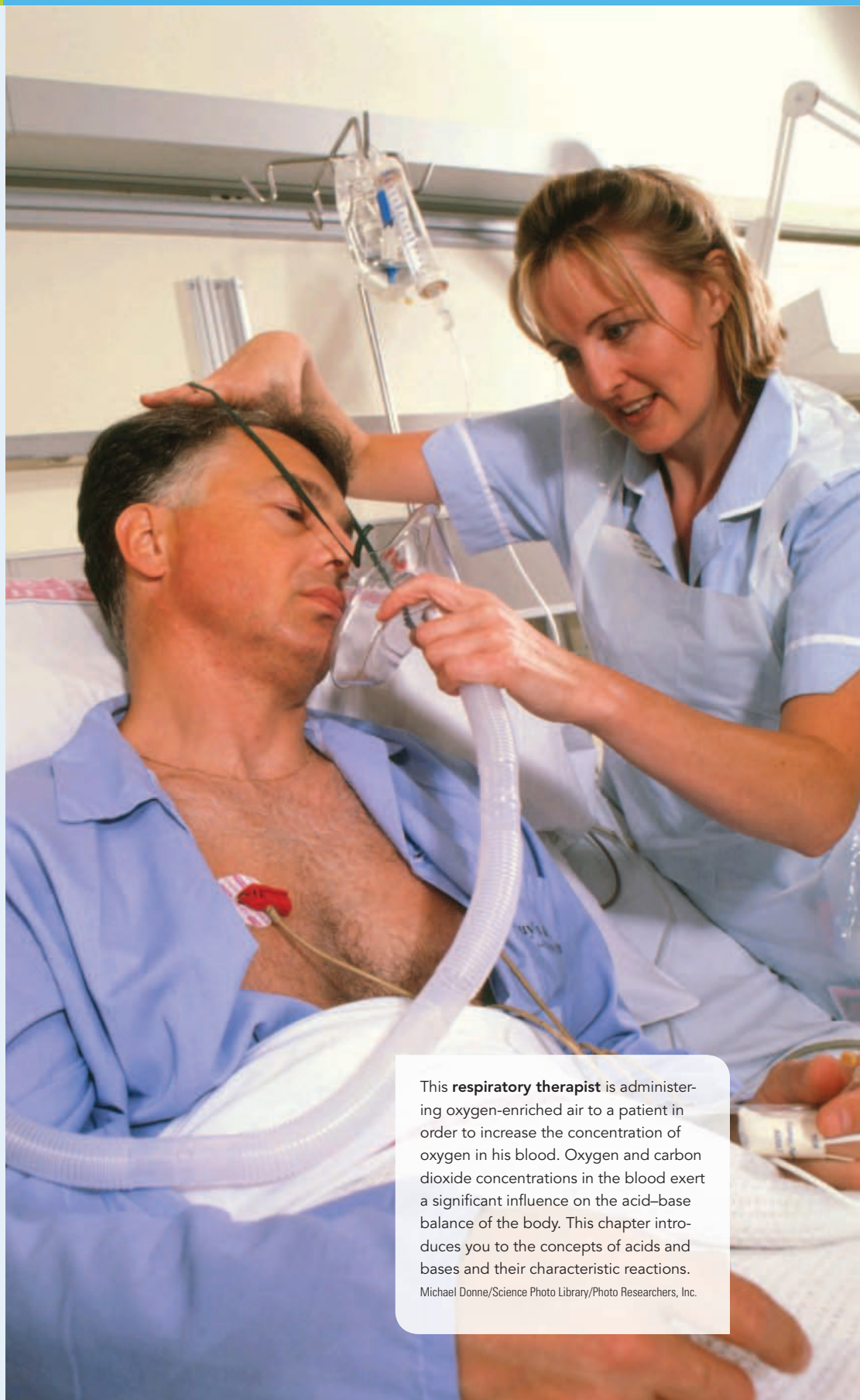
8.94 Someone once suggested that it is impossible to unscramble a scrambled egg. Describe an unscrambled and a scrambled egg in terms of the concept of entropy.

Learning Objectives

When you have completed your study of this chapter, you should be able to:

- 1 Write reaction equations that illustrate Arrhenius acid–base behavior. (Section 9.1)
- 2 Write reaction equations that illustrate Brønsted acid–base behavior, and identify Brønsted acids and bases from written reaction equations. (Section 9.2)
- 3 Name common acids. (Section 9.3)
- 4 Do calculations using the concept of the self-ionization of water. (Section 9.4)
- 5 Do calculations using the pH concept. (Section 9.5)
- 6 Write reaction equations that illustrate the characteristic reactions of acids. (Section 9.6)
- 7 Write reaction equations that represent neutralization reactions between acids and bases. (Section 9.7)
- 8 Write reaction equations that illustrate various ways to prepare salts, and do calculations using the concept of an equivalent of salt. (Section 9.8)
- 9 Demonstrate an understanding of the words *weak* and *strong* as applied to acids and bases. (Section 9.9)
- 10 Demonstrate an understanding of the titration technique used to analyze acids and bases. (Section 9.10)
- 11 Do calculations related to the analysis of acids and bases by titration. (Section 9.11)
- 12 Explain the concept of salt hydrolysis, and write equations to illustrate the concept. (Section 9.12)
- 13 Explain how buffers work, and write equations to illustrate their action. (Section 9.13)

OWL Online homework for this chapter may be assigned in OWL.



This **respiratory therapist** is administering oxygen-enriched air to a patient in order to increase the concentration of oxygen in his blood. Oxygen and carbon dioxide concentrations in the blood exert a significant influence on the acid–base balance of the body. This chapter introduces you to the concepts of acids and bases and their characteristic reactions.

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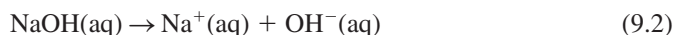
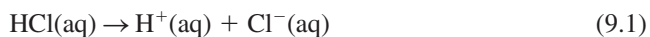
Acids, bases, and salts are among the most common and important solutes found in solutions. Until late in the 19th century, these substances were characterized by such properties as taste and color changes induced in certain dyes. Acids taste sour; bases, bitter; and salts, salty. Litmus, a dye, is red in the presence of acids and blue in the presence of bases. These and other observations led to the correct conclusions that acids and bases are chemical opposites, and that salts are produced when acids and bases react with each other. Today, acids and bases are defined in more precise ways that are useful when studying their characteristics.

9.1 The Arrhenius Theory

Learning Objective

1. Write reaction equations that illustrate Arrhenius acid–base behavior.

In 1887, Swedish chemist Svante Arrhenius proposed a theory dealing with electrolytic dissociation. He defined **acids** as substances that dissociate when dissolved in water and produce hydrogen ions (H^+). Similarly, **bases** are substances that dissociate and release hydroxide ions (OH^-) into the solution. Hydrogen chloride (HCl) and sodium hydroxide (NaOH) are examples of an Arrhenius acid and base, respectively. They dissociate in water as follows:



Note that the hydrogen ion is a bare proton, the nucleus of a hydrogen atom.

Arrhenius acid Any substance that provides H^+ ions when dissolved in water.

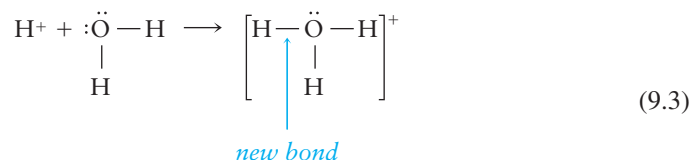
Arrhenius base Any substance that provides OH^- ions when dissolved in water.

9.2 The Brønsted Theory

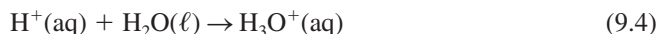
Learning Objective

2. Write reaction equations that illustrate Brønsted acid–base behavior, and identify Brønsted acids and bases from written reaction equations.

Arrhenius did not know that free hydrogen ions cannot exist in water. They covalently bond with water molecules to form hydronium ions (H_3O^+). The water molecules provide both electrons used to form the covalent bond:

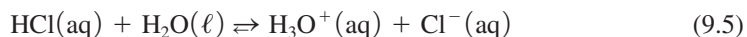


Or, more simply,



In 1923, Johannes Brønsted in Denmark and Thomas Lowry in England proposed an acid–base theory that took into account this behavior of hydrogen ions. They defined an **acid** as any hydrogen-containing substance that donates a proton (hydrogen ion) to another substance and a **base** as any substance that accepts a proton.

In conformity with this theory, the acidic behavior of covalently bonded HCl molecules in water is written



The HCl behaves as a Brønsted acid by donating a proton to a water molecule. The water molecule, by accepting the proton, behaves as a base.

Brønsted acid Any hydrogen-containing substance that is capable of donating a proton (H^+) to another substance.

Brønsted base Any substance capable of accepting a proton from another substance.

conjugate base The species remaining when a Brønsted acid donates a proton.

conjugate acid–base pair A Brønsted acid and its conjugate base.

The double arrows of unequal length in Equation 9.5 indicate that the reaction is reversible with the equilibrium lying far to the right. In actual water solutions, essentially 100% of the dissolved HCl is in the ionic form at equilibrium. Remember, both the forward and the reverse reactions are taking place at equilibrium (Section 8.6). When the reverse reaction occurs, hydronium ions donate protons to chloride ions to form HCl and H₂O molecules. Thus, H₃O⁺ behaves as a Brønsted acid, and Cl[−] behaves as a Brønsted base. We see from this discussion that when a substance like HCl behaves as a Brønsted acid by donating a proton, the species that remains (Cl[−]) is a Brønsted base. The Cl[−] is called the **conjugate base** of HCl. Every Brønsted acid and the base formed when it donates a proton is called a **conjugate acid–base pair**. Thus, in Equation 9.5, we see that HCl and Cl[−] form a conjugate acid–base pair, as do H₃O⁺ and H₂O for the reverse reaction. Notice that the acid and base in a conjugate acid–base pair differ only by a proton, H⁺.

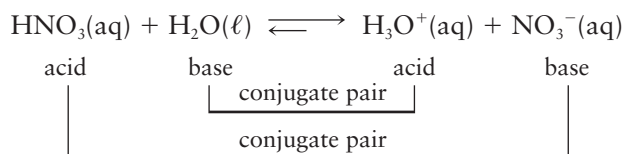
Example 9.1

Identify all Brønsted acids, bases, and acid–base conjugate pairs in the reactions represented by the following equations:

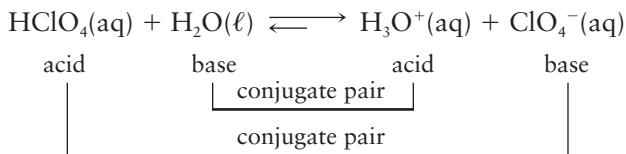
- $\text{HNO}_3(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$
- $\text{HClO}_4(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{ClO}_4^-(\text{aq})$
- $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{OH}^-(\text{aq}) + \text{NH}_4^+(\text{aq})$

Solution

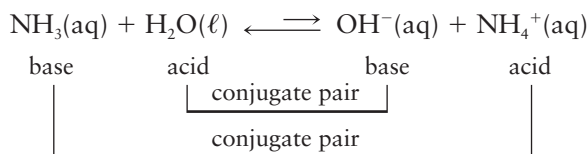
- a. Nitric acid, HNO₃, behaves as a Brønsted acid by donating a proton to H₂O, a base, in the forward reaction. In the reverse reaction, H₃O⁺, the conjugate acid of H₂O, donates a proton to NO₃[−], the conjugate base of HNO₃. In summary, the Brønsted acids are HNO₃ and H₃O⁺, the Brønsted bases are H₂O and NO₃[−], and the conjugate acid–base pairs are HNO₃/NO₃[−] and H₃O⁺/H₂O:



- b. Similarly, perchloric acid (HClO₄) is a Brønsted acid, and H₂O is a Brønsted base (forward reaction). Also, H₃O⁺ is a Brønsted acid, and the perchlorate ion (ClO₄[−]) is a Brønsted base (reverse reaction). The conjugate acid–base pairs are HClO₄/ClO₄[−] and H₃O⁺/H₂O:



- c. In this reaction, water donates a proton instead of accepting one. Therefore, H₂O is a Brønsted acid, and ammonia (NH₃) is a Brønsted base (forward reaction). The ammonium ion (NH₄⁺) is an acid, and the hydroxide ion (OH[−]) is a base (reverse reaction). Note that an Arrhenius base was a substance that released the OH[−], whereas according to Brønsted, the OH[−] is a base. The conjugate acid–base pairs are H₂O/OH[−] and NH₄⁺/NH₃:



► **Learning Check 9.1** Identify all Brønsted acids, bases, and acid–base conjugate pairs in the reactions represented by the following equations:

- $\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$
- $\text{NO}_2^-(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{HNO}_2(\text{aq}) + \text{OH}^-(\text{aq})$
- $\text{HS}^-(\text{aq}) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{S}^{2-}(\text{aq})$

9.3 Naming Acids

Learning Objective

3. Name common acids.

In Section 4.4, the rules for naming binary ionic compounds were given. The rules for naming binary covalent compounds and ionic compounds that contain polyatomic ions were discussed in Section 4.10. We now conclude our discussion of inorganic nomenclature by giving the rules used to name hydrogen-containing compounds that behave as acids. Examples of the two types of compounds that behave as acids were given in Section 9.2. Acids of the first type, represented by HCl , are compounds in which hydrogen is covalently bonded to a nonmetal. In acids of the second type, hydrogen is covalently bonded to a polyatomic ion. An example of the second type is HNO_3 .

You probably recognized that HCl is a binary covalent compound that can be named by the rules given earlier in Section 4.10. According to those rules, HCl should be named hydrogen chloride. In fact, that is the correct name for the compound HCl that has not been dissolved in water and is represented in reaction equations by the notation $\text{HCl}(\text{g})$. Such compounds that have not been dissolved in water are said to be anhydrous (without water). However, when the gas is dissolved in water and represented in equations by the notation $\text{HCl}(\text{aq})$, it behaves as an acid and is given another name. The following rules are used to name acidic water solutions of such compounds:

1. The word *hydrogen* in the anhydrous compound name is dropped.
2. The prefix *hydro-* is attached to the stem of the name of the nonmetal that is combined with hydrogen.
3. The suffix *-ide* on the stem of the name of the nonmetal that is combined with hydrogen is replaced with the suffix *-ic*.
4. The word *acid* is added to the end of the name as a separate word.

► Example 9.2

Determine the name that would be given to each of the following binary covalent compounds in the anhydrous form and in the form of water solutions:

- a. HCl (stomach acid)
- b. H_2S (a gas produced when some sulfur-containing foods such as eggs decay)

Solution

- a. The name of the anhydrous compound was given above as hydrogen chloride. The name of the water solution is obtained by dropping *hydrogen* from the anhydrous compound name and adding the prefix *hydro-* to the stem *chlor*. The *-ide* suffix on the *chlor* stem is replaced by the suffix *-ic* to give the name *hydrochloric*. The word *acid* is added, giving the final name *hydrochloric acid* for the water solution.
- b. According to the rules of Section 4.10, the anhydrous compound name is hydrogen sulfide. The first two steps in obtaining the name of the water solution are to drop *hydrogen* and to add the prefix *hydro-* to the stem *sulf*. However, in acids involving

sulfur as the nonmetal combined with hydrogen, the stem *sulf* is replaced by the entire name *sulfur* for pronunciation reasons. The next steps involve dropping the suffix *-ide*, adding the suffix *-ic*, and adding the word *acid*. The resulting name of the water solution is *hydrosulfuric acid*.

► **Learning Check 9.2** Determine the name that would be given to each of the following binary covalent compounds in the anhydrous form and in the form of water solutions:

- a. HI
- b. HBr

Acids of the second type, in which hydrogen is covalently bonded to a polyatomic ion, have the same name in the anhydrous form and in the form of water solutions. The names for these acids are based on the name of the polyatomic ion to which the hydrogen is bonded. The rules are as follows:

1. All hydrogens that are written as the first part of the formula of the acid are removed. The hydrogens are removed in the form of H^+ ions.
2. The polyatomic ion that remains after the H^+ ions are removed is named by referring to sources such as Table 4.7.
3. When the remaining polyatomic ion has a name ending in the suffix *-ate*, the suffix is replaced by the suffix *-ic*, and the word *acid* is added.
4. When the remaining polyatomic ion has a name ending in the suffix *-ite*, the suffix is replaced by the suffix *-ous*, and the word *acid* is added.
5. If the polyatomic ion contains sulfur or phosphorus, the stems *-sulf* or *-phosph* that remain in Steps 3 or 4, when the suffixes *-ate* or *-ite* are replaced, are expanded for pronunciation reasons to *-sulfur* and *-phosphor* before the *-ic* or *-ous* suffixes are added.

► Example 9.3

Compounds derived from the acid H_3PO_4 serve numerous important functions in the body, including the control of acidity in urine and body cells and the storage of energy in the form of ATP. Name this important acid.

Solution

The removal of the three H^+ ions leaves behind the PO_4^{3-} polyatomic ion. This ion is named the phosphate ion in Table 4.7. According to Rules 1–4, the *-ate* suffix is replaced by the *-ic* suffix to give the name *phosphic acid*. However, Rule 5 must be used for this phosphorus-containing acid. The stem is expanded to *phosphor* to give the final name, *phosphoric acid*.

► **Learning Check 9.3** The acid H_2CO_3 is involved in many processes in the body, including the removal of CO_2 gas produced by cellular metabolism and the control of the acidity of various body fluids. Name this important acid.

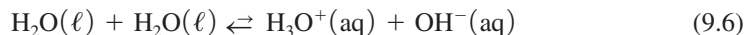
9.4 The Self-Ionization of Water

Learning Objective

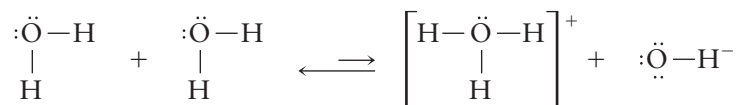
4. Do calculations using the concept of the self-ionization of water.

In Examples 9.1a and b, water behaved as a Brønsted base. In Example 9.1c, it was a Brønsted acid. But what happens when only pure water is present? The answer is that

water behaves as both an acid and a base and undergoes a self- or auto-ionization. The equation representing this self-ionization is



or



The transfer of a proton from one water molecule (the acid) to another (the base) causes one H_3O^+ and one OH^- to form. Therefore, in pure water the concentrations of H_3O^+ and OH^- must be equal. At 25°C these concentrations are 10^{-7} mol/L (M). Thus, the equilibrium position is far to the left, as indicated by the arrows in Equation 9.6. Unless noted otherwise, all concentrations and related terms in this chapter are given at 25°C .

The term **neutral** is used to describe any water solution in which the concentrations of H_3O^+ and OH^- are equal. Thus, pure water is neutral because each liter of pure water contains 10^{-7} mol H_3O^+ and 10^{-7} mol OH^- , at equilibrium. Although all water solutions are not necessarily neutral, it is true that in any solution that contains water, the product of the molar concentrations of H_3O^+ and OH^- is a constant. This becomes apparent by writing the equilibrium expression for Reaction 9.6:

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{H}_2\text{O}]} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \quad (9.7)$$

This expression contains the square of the concentration of water in the denominator. However, only a tiny amount of water actually reacts to form H_3O^+ and OH^- (10^{-7} mol/L), so the concentration of water remains essentially constant. Rearrangement of Equation 9.7 gives

$$K[\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-] \quad (9.8)$$

This equation may be written as

$$K[\text{H}_2\text{O}]^2 = K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad (9.9)$$

where K_w is a new constant called the **ion product of water**. It is a constant because it is equal to the product of two constants, K and $[\text{H}_2\text{O}]^2$. At 25°C , K_w can be evaluated from the measured values of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ in pure water.

$$\begin{aligned} K_w &= [\text{H}_3\text{O}^+][\text{OH}^-] = (1.0 \times 10^{-7} \text{ mol/L})(1.0 \times 10^{-7} \text{ mol/L}) \\ &= 1.0 \times 10^{-14} (\text{mol/L})^2 \end{aligned} \quad (9.10)$$

Equation 9.10 is valid not only for pure water but for any solution in which water is the solvent. Notice that we are including units for equilibrium constants in this discussion. This makes the calculation of concentrations easier to follow and understand.

A solution is classified as **acidic** when the concentration of H_3O^+ is greater than the concentration of OH^- . In a **basic** or **alkaline solution**, the concentration of OH^- is greater than that of H_3O^+ . However, the product of the molar concentrations of H_3O^+ and OH^- will be $1.0 \times 10^{-14} (\text{mol/L})^2$ in either case. Many acidic and basic materials are found in the home (see ► Figure 9.1).

neutral A term used to describe any water solution in which the concentrations of H_3O^+ and OH^- are equal. Also, a water solution with pH = 7.

ion product of water The equilibrium constant for the dissociation of pure water into H_3O^+ and OH^- .

acidic solution A solution in which the concentration of H_3O^+ is greater than the concentration of OH^- . Also, a solution in which pH is less than 7.

basic or alkaline solution A solution in which the concentration of OH^- is greater than the concentration of H_3O^+ . Also, a solution in which pH is greater than 7.

Figure 9.1 Acidic and basic materials are common in the home. Look at the photos, and note a single category to which most of the acidic materials belong, and one to which most of the basic materials belong.



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1

Acidic materials found in the home.



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2

Basic or alkaline materials found in the home.

Example 9.4

Classify each of the following solutions as acidic, basic, or neutral. Calculate the molar concentration of the ion whose concentration is not given.

- $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-4} \text{ mol/L}$
- $[\text{OH}^-] = 1.0 \times 10^{-9} \text{ mol/L}$
- $[\text{OH}^-] = 1.0 \times 10^{-6} \text{ mol/L}$

Solution

- Because $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-4} \text{ mol/L}$, a rearrangement of Equation 9.10 gives

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14} (\text{mol/L})^2}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14} (\text{mol/L})^2}{1.0 \times 10^{-4} \text{ mol/L}} \\ = 1.0 \times 10^{-10} \text{ mol/L}$$

Thus,

$$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-4} \text{ mol/L} \quad \text{and}$$

$$[\text{OH}^-] = 1.0 \times 10^{-10} \text{ mol/L}$$

The solution is acidic because the $[\text{H}_3\text{O}^+]$ is greater than the $[\text{OH}^-]$; 1.0×10^{-4} is greater than 1.0×10^{-10} .

- Similarly, $[\text{OH}^-] = 1.0 \times 10^{-9} \text{ mol/L}$; therefore,

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14} (\text{mol/L})^2}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14} (\text{mol/L})^2}{1.0 \times 10^{-9} \text{ mol/L}} \\ = 1.0 \times 10^{-5} \text{ mol/L}$$

This solution is also acidic because 1.0×10^{-5} is greater than 1.0×10^{-9} .

- $[\text{OH}^-] = 1.0 \times 10^{-6} \text{ mol/L}$; therefore,

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14} (\text{mol/L})^2}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14} (\text{mol/L})^2}{1.0 \times 10^{-6} \text{ mol/L}} \\ = 1.0 \times 10^{-8} \text{ mol/L}$$

This solution is basic because the OH^- concentration ($1.0 \times 10^{-6} \text{ mol/L}$) is greater than the H_3O^+ concentration ($1.0 \times 10^{-8} \text{ mol/L}$).

► **Learning Check 9.4** Classify each of the following solutions as acidic, basic, or neutral. Calculate the molarity of the ion whose concentration is not given.

- a. $[\text{OH}^-] = 1.0 \times 10^{-5} \text{ mol/L}$
- b. $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-9} \text{ mol/L}$
- c. $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-2} \text{ mol/L}$

9.5 The pH Concept

Learning Objective

5. Do calculations using the pH concept.

In Section 9.4, you learned that the concentration of H_3O^+ in pure water is $1.0 \times 10^{-7} \text{ M}$. Chemists, technologists, and other laboratory personnel routinely work with solutions in which the H_3O^+ concentration may be anywhere from 10 to 10^{-14} M . Because of the inconvenience of working with numbers that extend over such a wide range, chemists long ago adopted a shortcut notation known as the pH. Mathematically, the **pH** is defined in terms of the negative logarithm (\log) of $[\text{H}_3\text{O}^+]$ by the following two equations, where we now introduce the common practice of substituting H^+ for H_3O^+ to simplify equations:

$$\text{pH} = -\log[\text{H}^+] \quad (9.11)$$

$$[\text{H}^+] = 1 \times 10^{-\text{pH}} \quad (9.12)$$

Thus, pH is simply the negative of the exponent used to express the hydrogen-ion concentration in moles per liter.

pH The negative logarithm of the molar concentration of H^+ (H_3O^+) in a solution.

► Example 9.5

Express the following concentrations in terms of pH:

- a. $[\text{H}^+] = 1 \times 10^{-5} \text{ mol/L}$
- b. $[\text{OH}^-] = 1 \times 10^{-9} \text{ mol/L}$
- c. $[\text{H}^+] = 1 \times 10^{-7} \text{ mol/L}$
- d. $[\text{H}^+] = 1 \times 10^{-11} \text{ mol/L}$

Solution

- a. pH is the negative of the exponent used to express $[\text{H}^+]$. Therefore, $\text{pH} = -(-5) = 5.0$
- b. Here $[\text{OH}^-]$ is given, and $[\text{H}^+]$ must be calculated. We remember Equation 9.10 and get

$$[\text{H}^+] = \frac{1.0 \times 10^{-14} (\text{mol/L})^2}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14} (\text{mol/L})^2}{1 \times 10^{-9} \text{ mol/L}} = 1 \times 10^{-5} \text{ mol/L}$$

Therefore, $\text{pH} = -(-5) = 5.0$

- c. This $\text{pH} = -(-7) = 7.0$. $[\text{H}^+] = 1 \times 10^{-7} \text{ mol/L}$ and corresponds to pure water and neutral solutions. Thus, a pH of 7 represents neutrality.
- d. $\text{pH} = -(-11) = 11.0$

► **Learning Check 9.5** Express the following concentrations in terms of pH.

- a. $[\text{H}^+] = 1 \times 10^{-14} \text{ mol/L}$
- b. $[\text{OH}^-] = 1.0 \text{ mol/L}$
- c. $[\text{OH}^-] = 1 \times 10^{-8} \text{ mol/L}$

Table 9.1 Relationships Between $[H^+]$, $[OH^-]$, and pH

	$[H^+]$	$[OH^-]$	pH	Examples (solids are dissolved in water)
<i>Neutral</i>	10^0	10^{-14}	0	HCl (1 mol/L)
	10^{-1}	10^{-13}	1	Gastric juice
	10^{-2}	10^{-12}	2	Lemon juice
	10^{-3}	10^{-11}	3	Vinegar, carbonated drink Aspirin
	10^{-4}	10^{-10}	4	Orange juice Apple juice
	10^{-5}	10^{-9}	5	Black coffee
	10^{-6}	10^{-8}	6	Normal urine (average value) Milk, liquid dishwashing detergent
	10^{-7}	10^{-7}	7	Saliva, pure water Blood
	10^{-8}	10^{-6}	8	Soap (not synthetic detergent) Baking soda Phosphate-containing detergent
	10^{-9}	10^{-5}	9	Milk of magnesia Powdered household cleanser
	10^{-10}	10^{-4}	10	Phosphate-free detergent
	10^{-11}	10^{-3}	11	Household ammonia Liquid household cleaner
	10^{-12}	10^{-2}	12	
	10^{-13}	10^{-1}	13	NaOH (0.1 mol/L)
	10^{-14}	10^0	14	NaOH (1 mol/L)

The pH value of 5.0 obtained in Example 9.5a corresponds to a solution in which the H^+ concentration is greater than the OH^- concentration. Thus, the solution is acidic. Any solution with a pH less than 7 is classified as acidic. Any solution with a pH greater than 7 is classified as basic or alkaline. The pH values of some familiar solutions are given in Table 9.1.

Example 9.6

Determine the H^+ and OH^- molar concentrations that correspond to the following pH values:

- pH = 9.0
- pH = 3.0
- pH = 11.0

Solution

In each case, the relationships $[H^+] = 1 \times 10^{-\text{pH}}$ and $K_w = [H^+][OH^-] = 1.0 \times 10^{-14} (\text{mol/L})^2$ can be used. Note that we have substituted $[H^+]$ for $[H_3O^+]$ in Equation 9.10.

a. Because $\text{pH} = 9.0$, $[\text{H}^+] = 1 \times 10^{-\text{pH}} = 1 \times 10^{-9} \text{ mol/L}$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14} (\text{mol/L})^2}{1 \times 10^{-9} \text{ mol/L}} = 1 \times 10^{-5} \text{ mol/L}$$

b. Because $\text{pH} = 3.0$, $[\text{H}^+] = 1 \times 10^{-\text{pH}} = 1 \times 10^{-3} \text{ mol/L}$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14} (\text{mol/L})^2}{1 \times 10^{-3} \text{ mol/L}} = 1 \times 10^{-11} \text{ mol/L}$$

c. Because $\text{pH} = 11.0$, $[\text{H}^+] = 1 \times 10^{-\text{pH}} = 1 \times 10^{-11} \text{ mol/L}$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14} (\text{mol/L})^2}{1 \times 10^{-11} \text{ mol/L}} = 1 \times 10^{-3} \text{ mol/L}$$

► **Learning Check 9.6** Determine the $[\text{H}^+]$ and $[\text{OH}^-]$ values that correspond to the following pH values:

a. $\text{pH} = 10.0$

b. $\text{pH} = 4.0$

c. $\text{pH} = 5.0$

It is apparent from Table 9.1 that not all solutions have pH values that are neat whole numbers. For example, the pH of vinegar is about 3.3. How do we deal with such numbers? The H^+ concentration of vinegar could be written $1 \times 10^{-3.3}$, but it is not convenient to work with exponents that are not whole numbers. When exact values are not needed, the pH, $[\text{H}^+]$, and so on can be expressed as a range. Thus, the H^+ concentration of vinegar is between 1×10^{-3} and $1 \times 10^{-4} \text{ mol/L}$. Similarly, a solution with $[\text{H}^+] = 2 \times 10^{-5} \text{ mol/L}$ has a pH between 4 and 5.

When more exact values are needed, we must work with logarithms. This is most easily done by using a hand calculator. A hydrogen-ion concentration is converted to pH by taking the logarithm and changing its sign. ► Table 9.2 gives the steps of a typical calculator procedure (what button is pushed, etc.) and a typical calculator readout or display for the conversion of $[\text{H}^+] = 3.6 \times 10^{-4} \text{ mol/L}$ into pH. The pH from Table 9.2 would be recorded as 3.44.

► **Learning Check 9.7** Convert the following $[\text{H}^+]$ values into pH:

a. $[\text{H}^+] = 4.2 \times 10^{-5} \text{ mol/L}$

b. $[\text{H}^+] = 8.1 \times 10^{-9} \text{ mol/L}$

Calculators can also be used to convert pH values into corresponding molar concentrations. The steps are given in ► Table 9.3 for the conversion of a pH value of 5.92 into

Table 9.2 Calculating pH from Molarity with a Calculator

Step	Calculator Procedure	Calculator Display
1. Enter 3.6	Press buttons 3, ., 6	3.6
2. Enter 10^{-4}	Press button that activates exponential mode (EE, Exp, etc.)	3.6^{00}
	Press 4	3.6^{04}
	Press change-sign button (\pm , etc.)	3.6^{-04}
3. Take logarithm	Press log button (log, etc.)	-3.4437
4. Change sign	Press change-sign button (\pm , etc.)	3.4437

Table 9.3 Calculating Molarity from pH with a Calculator

Step	Calculator Procedure	Calculator Display
1. Enter 5.92	Press 5, ., 9, 2	5.92
2. Change sign	Press change-sign button (\pm , etc.)	-5.92
3. Take antilog	Press antilog or 10^x button, or (more commonly) press inv. or 2^{nd} function button and then log button	.0000012 or 1.2^{-06}

$[\text{H}^+]$. As shown in Table 9.3, a pH of 5.92 corresponds to a $[\text{H}^+]$ of 1.2×10^{-6} mol/L. Note that the number of figures to the right of the decimal in a pH value should be the same as the number of significant figures in the $[\text{H}^+]$ value. Thus, the two figures to the right of the decimal in $\text{pH} = 5.92$ is reflected in the two significant figures in $[\text{H}^+] = 1.2 \times 10^{-6}$ mol/L.

► **Learning Check 9.8** Convert the following pH values into molar concentrations of H^+ :

- $\text{pH} = 2.75$
- $\text{pH} = 8.33$

9.6 Properties of Acids

Learning Objective

- Write reaction equations that illustrate the characteristic reactions of acids.

Acids and bases are used so often in most laboratories that stock solutions are kept readily available at each work space. The common solutions, their concentrations, and label designations are given in ► Table 9.4.

Table 9.4 Common Laboratory Acids and Bases

Name	Formula	Label Concentration	Molarity
<i>Acids</i>			
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	Glacial	18
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	Dilute	6
Hydrochloric acid	HCl	Concentrated	12
Hydrochloric acid	HCl	Dilute	6
Nitric acid	HNO_3	Concentrated	16
Nitric acid	HNO_3	Dilute	6
Sulfuric acid	H_2SO_4	Concentrated	18
Sulfuric acid	H_2SO_4	Dilute	3
<i>Bases</i>			
Aqueous ammonia ^a	NH_3	Concentrated	15
Aqueous ammonia	NH_3	None usually given	6
Sodium hydroxide	NaOH	None usually given	6

^aOften erroneously called ammonium hydroxide and given the formula NH_4OH .

Example 9.7

Describe how you would make 250 mL of 1 M HNO_3 by using a dilute HNO_3 stock solution.

Solution

According to Table 9.4, the dilute HNO_3 stock solution is 6 M. The volume of 6 M HNO_3 needed to make 250 mL of 1 M HNO_3 is obtained by using Equation 7.9. It must be remembered that this equation is useful only for dilution problems such as this one. The equation is not useful for calculations involving the volume of one solution that will react with a specific volume of a second solution (Sections 9.10 and 9.11).

$$C_c V_c = C_d V_d$$

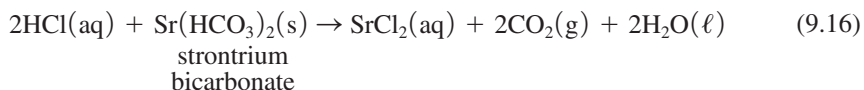
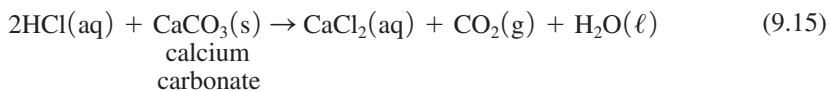
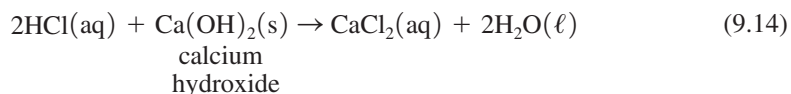
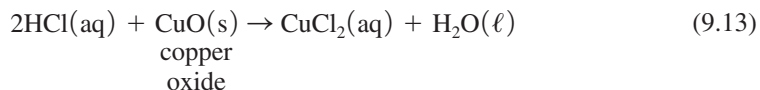
$$(6 \text{ M}) V_c = (1 \text{ M})(250 \text{ mL})$$

$$V_c = \frac{(1 \text{ M})(250 \text{ mL})}{6 \text{ M}} = 41.7 \text{ mL}$$

Because the molarity is given using only one significant figure, the solution can be made without too much attention to volumetric flasks and the like. Thus, 42 mL of 6 M HNO_3 is measured with a graduated cylinder, and this is added to 208 mL of distilled water that has also been measured with a graduated cylinder.

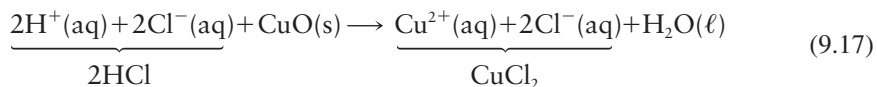
Learning Check 9.9 Describe how you would prepare 500 mL of 3.0 M aqueous ammonia using a concentrated NH_3 stock solution (Table 9.4).

Different acids have different properties that make some more practical than others for specific uses. However, all acids have certain properties in common. Two of these were mentioned earlier—all acids taste sour and produce H_3O^+ ions when dissolved in water. In addition, all acids undergo characteristic double-replacement reactions with solid oxides, hydroxides, carbonates, and bicarbonates (see Figure 9.2).

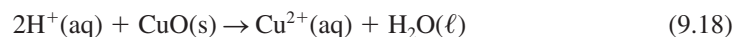


Notice that the preceding reactions are written using molecular equations (Section 5.7).

Reactions involving ionic substances can also be written as total ionic equations or net ionic equations. Equation 9.13 is written in total ionic form in Equation 9.17.



We see that the chloride ions are spectator ions, so a net ionic equation can be written as shown in Equation 9.18.



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1 Marble, a naturally occurring form of CaCO_3 , reacts with hydrochloric acid, HCl . What gas is produced?



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2 Eggshells are also made of CaCO_3 .

Figure 9.2 The reaction of hydrochloric acid with two natural forms of calcium carbonate (CaCO_3).

The general nature of the reaction is emphasized in the net ionic form because the H^+ could come from any acid.

Remember that correctly written molecular equations must have their atoms balanced (Section 5.1). Total ionic and net ionic equations must also have their atoms balanced, but in addition the total charges on each side of the equation must balance. In Equation 9.18, for example, the two H^+ ions provide two positive charges on the left, which are balanced by the two positive charges of Cu^{2+} on the right.

Example 9.8

Write Equations 9.14 and 9.15 in total ionic and net ionic forms.

Solution

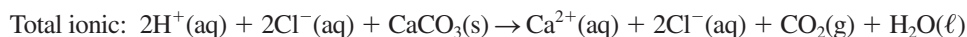
In Equation 9.14, HCl and CaCl_2 are soluble and ionizable.



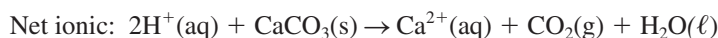
The Cl^- is a spectator ion.



In Equation 9.15, HCl and CaCl_2 are soluble and ionizable.

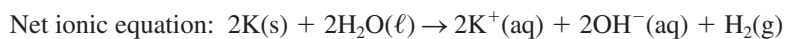
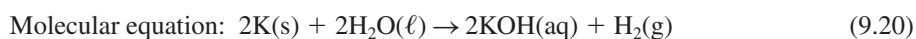
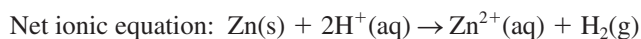
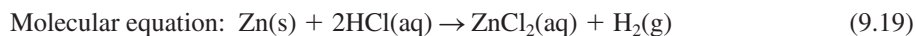


Again, Cl^- is a spectator ion.



Learning Check 9.10 Write Equation 9.16 in total and net ionic forms. Consider HCl and SrCl_2 as soluble and ionizable.

Another property of acids is their ability to react with (and dissolve) certain metals to yield hydrogen gas. This is a redox reaction (Section 5.3), as evidenced by the change in oxidation number of hydrogen as the reaction takes place. In compounds such as acids, hydrogen has an oxidation number of +1. In hydrogen gas, the oxidation number is 0 (Section 5.3). Thus, hydrogen is reduced during the reaction, and, as shown by Equations 9.19 and 9.20, the metal is oxidized. The ability to reduce hydrogen ions to hydrogen gas is not the same for all metals. Some are such strong reducing agents that they can react with hydrogen ions of very low concentrations such as that found in water. Others are so weak as reducing agents that they cannot react with H^+ at the high concentration found in concentrated acids. These tendencies are represented by the **activity series** of metals shown in Table 9.5. The higher a metal is in the series, the more active it is as a reducing agent. Some typical reactions are given in Equations 9.19 and 9.20 (see Figure 9.3):



Learning Check 9.11 Write molecular, total ionic, and net ionic equations to represent the following reactions:

- Calcium (Ca) with cold water (NOTE: $\text{Ca}(\text{OH})_2$ is not soluble in water.)
- Mg with H_2SO_4 (NOTE: MgSO_4 is soluble and ionizable in water.)

activity series A tabular representation of the tendencies of metals to react with H^+ .

Table 9.5 The Activity Series of the Metals

Metal	Symbol	Comments
Potassium	K	} React violently with cold water
Sodium	Na	
Calcium	Ca	Reacts slowly with cold water
Magnesium	Mg	} React very slowly with steam, but quite rapidly in higher H^+ concentrations
Aluminum	Al	
Zinc	Zn	
Chromium	Cr	
Iron	Fe	} React in moderately high H^+ concentrations
Nickel	Ni	
Tin	Sn	
Lead	Pb	
Copper	Cu	} Do not react with H^+
Mercury	Hg	
Silver	Ag	
Platinum	Pt	
Gold	Au	

9.7 Properties of Bases

Learning Objective

7. Write reaction equations that represent neutralization reactions between acids and bases.

Solutions containing bases feel soapy or slippery and change the color of litmus from red to blue. Equation 9.14 illustrates their most characteristic chemical property—they react readily with acids. In most of the earliest acid–base reactions studied, the complete reaction of an acid with a base produced a neutral solution. For this reason, such

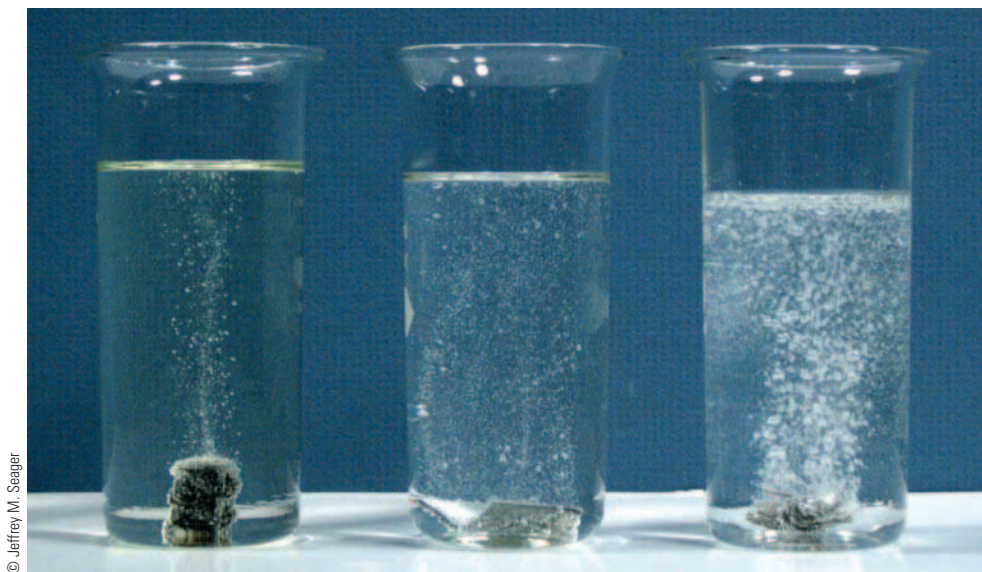
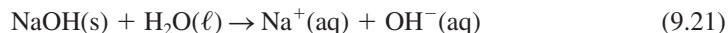


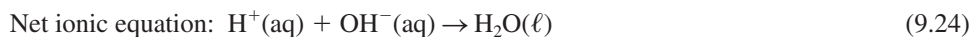
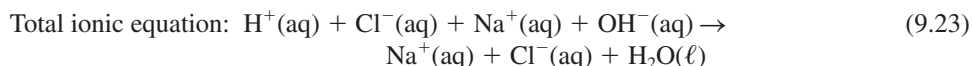
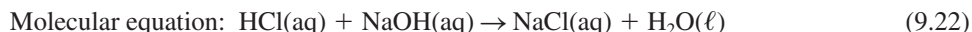
Figure 9.3 Metals vary in their ability to reduce hydrogen ions (H^+) to hydrogen gas (H_2). This difference is apparent when iron, zinc, and magnesium (left to right) are put into hydrochloric acid (HCl) of the same molarity. Are these results consistent with Table 9.5? Explain.

neutralization reaction A reaction in which an acid and base react completely, leaving a solution that contains only a salt and water.

reactions were often called **neutralization reactions** (see below). It is now known that many “neutralization” reactions do not produce neutral solutions (Section 9.12). However, the name for the reactions is still used. More than 20 billion pounds of sodium hydroxide (NaOH) is produced and used in the United States each year. This useful crystalline solid is quite soluble in water and dissociates to form basic solutions.



The neutralization reaction between NaOH and HCl is



The molecular equation (9.22) illustrates the following statement, which is a common definition of neutralization: During a neutralization reaction, an acid and a base combine to form a salt and water. (More is said about salts in the next section.) The net ionic form of the equation (9.24) emphasizes the general nature of neutralization reactions: H^+ ions (from any source) react with OH^- (from any source) to form water.

Bases also react with fats and oils and convert them into smaller, soluble molecules. For this reason, most household cleaning products contain basic substances. For example, lye (NaOH) is the active ingredient in numerous drain cleaners, and many liquid household cleaners contain ammonia.

► **Learning Check 9.12** Write molecular, total ionic, and net ionic equations to represent neutralization reactions between the following acids and bases:

- a. HNO_3 and NaOH
- b. H_2SO_4 and KOH

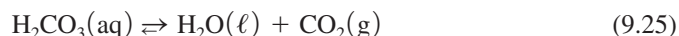
9.8 Salts

Learning Objective

8. Write reaction equations that illustrate various ways to prepare salts, and do calculations using the concept of an equivalent of salt.

At room temperature, **salts** are solid ionic compounds that contain the **cation** (positive ion) of a base and the **anion** (negative ion) of an acid. Thus, ordinary table salt (NaCl) contains Na^+ , the cation of NaOH, and Cl^- , the anion of HCl (look again at Equation 9.22). Similarly, CuSO_4 is a salt containing the cation of Cu(OH)_2 and the anion of H_2SO_4 . You must be careful to think of the term *salt* in a general way, and not as representing only table salt (NaCl).

Some acids and bases are not stable enough to be isolated even though their salts are. For example, carbonic acid (H_2CO_3) cannot be isolated in the pure state. When it forms in water, it promptly decomposes:



Despite this characteristic, salts of carbonic acid, such as Na_2CO_3 and NaHCO_3 , are quite stable.

It is not necessary to identify the parent acid and base in order to write correct salt formulas or names. Just remember that the cation of a salt can be any positive ion except H^+ , and it will usually be a simple metal ion or NH_4^+ . The salt anion can be any negative ion except OH^- . Most of the polyatomic anions you will use were given earlier in Table 4.7. The rules for naming salts were given in Sections 4.4 and 4.10.

salt A solid crystalline ionic compound at room temperature that contains the cation of a base and the anion of an acid.

cation A positively charged ion.

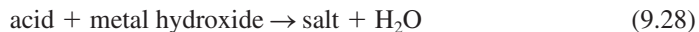
anion A negatively charged ion.

Table 9.6 Some Useful and Common Hydrates

Formula	Chemical Name	Common Name	Uses
$\text{CaSO}_4 \cdot \text{H}_2\text{O}$	Calcium sulfate monohydrate	Plaster of Paris	Plaster, casts, molds
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Calcium sulfate dihydrate	Gypsum	Casts, molds, wallboard
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Magnesium sulfate heptahydrate	Epsom salts	Cathartic
$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	Sodium tetraborate decahydrate	Borax	Laundry
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	Sodium carbonate decahydrate	Washing soda	Water softener
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	Sodium phosphate dodecahydrate	Trisodium phosphate (TSP)	Water softener
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	Sodium sulfate decahydrate	Glauber's salt	Cathartic
$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	Sodium thiosulfate pentahydrate	Hypo	Photography

As previously observed, salts dissolved in solution are dissociated into ions. The salt can be recovered by evaporating away the water solvent. When this is done carefully, some salts retain specific numbers of water molecules as part of the solid crystalline structure. Such salts are called **hydrates**, and the retained water is called the **water of hydration**. Most hydrates lose all or part of the water of hydration when they are heated to moderate or high temperatures. A number of useful hydrates are given in Table 9.6.

Many salts occur in nature, and some are used as industrial raw materials. Examples are sodium chloride, NaCl (a source of Cl_2 and NaOH); calcium carbonate or limestone, CaCO_3 (a source of cement and building stone); and calcium phosphate or rock phosphate, $\text{Ca}_3(\text{PO}_4)_2$ (a source of fertilizer). In the laboratory, salts can be prepared by reacting a solution of an appropriate acid with a metal, a metal oxide, a metal hydroxide, a metal carbonate, or a metal bicarbonate. These reactions, given earlier as examples of acid properties (Equations 9.19, 9.13, 9.14, 9.15, 9.16), are given below in a general form:

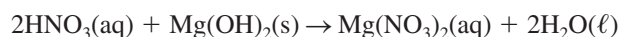
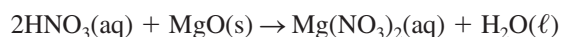
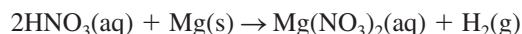


Example 9.9

Write equations to represent the preparation of $\text{Mg}(\text{NO}_3)_2$, using Reactions 9.26 through 9.30. Use molecular equations to emphasize the salt formation.

Solution

In each case, a dilute solution of nitric acid (HNO_3) is reacted with magnesium metal or the appropriate magnesium compound:



hydrate A salt that contains specific numbers of water molecules as part of the solid crystalline structure.

water of hydration Water retained as part of the solid crystalline structure of some salts.