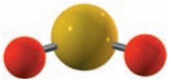
than 100 years elapsed before a careful reanalysis of the composition of air using multiple experimental techniques showed that oxygen and nitrogen account for only about 99% of the total volume, most of the remaining 1% being a new gas, given the name "argon." The other noble gases (helium, neon, krypton, and xenon) are present in air to lesser extents.

Other gases are found on the surface of the earth and in the atmosphere. Methane (CH_4), formerly known as "marsh gas," is produced by bacterial processes, especially in swampy areas. It is a major constituent of natural-gas deposits formed over many millennia by decay of plant matter beneath the surface of the earth. Recovery of methane from municipal landfills for use as a fuel is now a commercially feasible process. Gases also form when liquids evaporate. The most familiar example is water vapor in the air from the evaporation of liquid water; it provides the humidity of air.

Carbon dioxide, CO_2, is dissolved in aqueous solution to form carbonated beverages. Carbon dioxide also reacts with water to produce $H_2CO_3(aq)$, which provides some of the acidity in soft drinks. Solid carbon dioxide (dry ice) is used for refrigeration.



Sulfur dioxide, SO_2, is produced by burning sulfur in air as the first step in the production of sulfuric acid.

Sulfur trioxide, SO_3, is a corrosive gas produced by the further oxidation of sulfur dioxide.

Gases are also formed by chemical reactions. Some solids decompose upon heating to give gaseous products. One famous example is the decomposition of mercury(II) oxide to mercury and oxygen (Fig. 1.6):

$$2\ HgO(s) \xrightarrow{\text{Heat}} 2\ Hg(\ell) + O_2(g)$$

Joseph Priestly discovered the element oxygen while investigating this reaction. Even earlier, in 1756, Joseph Black showed that marble, which consists primarily of calcium carbonate ($CaCO_3$), decomposes upon heating to give quicklime (CaO) and carbon dioxide:

$$CaCO_3(s) \xrightarrow{\text{Heat}} CaO(s) + CO_2(g)$$

Ammonium chloride (NH_4Cl) decomposes under heat to produce two gases: ammonia and hydrogen chloride:

$$NH_4Cl(s) \xrightarrow{\text{Heat}} NH_3(g) + HCl(g)$$

Some gas-forming reactions proceed explosively. The decomposition of nitroglycerin is a detonation in which all the products are gases:

$$4\ C_3H_5(NO_3)_3(\ell) \longrightarrow 6\ N_2(g) + 12\ CO_2(g) + O_2(g) + 10\ H_2O(g)$$

Several elements react with oxygen to form gaseous oxides. Carbon dioxide forms during animal respiration and is also produced by burning coal, oil, and other materials that contain carbon compounds. The role of carbon dioxide in global warming is the subject of intense research and policy debates. Oxides of sulfur are produced by burning elemental sulfur, and oxides of nitrogen arise from combustion of elemental nitrogen. Sulfur is a common impurity in fossil fuels, and nitrogen is burned in high-temperature environments like automobile engines:

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$
$$2\ SO_2(g) + O_2(g) \longrightarrow 2\ SO_3(g)$$
$$N_2(g) + O_2(g) \longrightarrow 2\ NO(g)$$
$$2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g)$$

The role of these compounds in air pollution is described in Section 20.5.

Gases can also be produced by the reactions of acids with ionic solids. Carbon dioxide is produced by the reaction of acids with carbonates (Fig. 9.1):

$$CaCO_3(s) + 2\ HCl(g) \longrightarrow CaCl_2(s) + CO_2(g) + H_2O(\ell)$$

Other examples of this type of reaction include:

$$Na_2S(s) + 2\ HCl(g) \longrightarrow 2\ NaCl(s) + H_2S(g)$$
$$K_2SO_3(s) + 2\ HCl(g) \longrightarrow 2\ KCl(s) + SO_2(g) + H_2O(\ell)$$
$$NaCl(s) + H_2SO_4(\ell) \longrightarrow NaHSO_4(s) + HCl(g)$$

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FIGURE 9.1 The calcium carbonate in a piece of chalk reacts with an aqueous solution of hydrochloric acid to produce bubbles of carbon dioxide.

In these reactions, the metal ions (sodium, calcium, and potassium) play no direct role; so, parallel reactions can be written for other metal ions.

The gases mentioned earlier vary greatly in their chemical properties. Some, such as HCl and SO_3, are reactive, acidic, and corrosive, whereas others, such as N_2O and N_2, are much less reactive. While the chemical properties of gases vary significantly, their physical properties are quite similar and much simpler to understand. At sufficiently low densities, all gases behave physically in the same way. Their properties are summarized and interpreted by a model system called the "ideal" gas, which is the subject of the following sections.

9.2 Pressure and Temperature of Gases

The macroscopic behavior of a fixed mass of a gas is completely characterized by three properties: volume (V), pressure (P), and temperature (T). Volume is self-evident and needs no comment; as stated in Section 2.1, we use the liter as a unit of volume. The definition of pressure and temperature require a little more care.

Pressure and Boyle's Law

The force exerted by a gas on a unit area of the walls of its container is called the **pressure** of that gas. We do not often stop to think that the air around us exerts a pressure on us and on everything else at the surface of the earth. Evangelista Torricelli (1608–1647), an Italian scientist who had been an assistant to Galileo, demonstrated this phenomenon in an ingenious experiment. He sealed a long glass tube at one end and filled it with mercury. He then covered the open end with his thumb, turned the tube upside down, and immersed the open end in a dish of liquid mercury (Fig. 9.2a), taking care that no air leaked in. The mercury in the tube fell, leaving a nearly perfect vacuum at the closed end, but it did not all run out of the tube. It stopped when its top was about 76 cm above the level of the mercury in the dish. Torricelli showed that the exact height varied somewhat from day to day and from place to place.

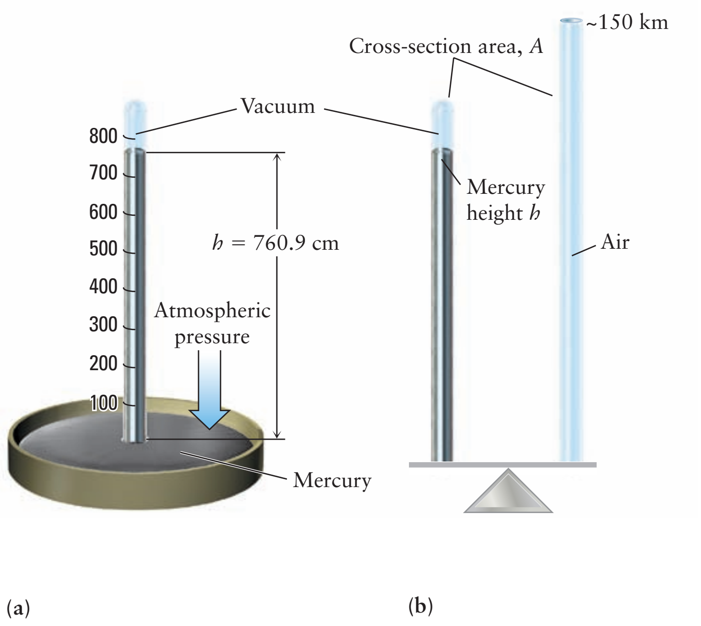

FIGURE 9.2 (a) In Torricelli's barometer, the top of the mercury in the tube is approximately 76 cm higher than that in the open beaker. (b) The mass of mercury in the column of height h exactly balances that of a column of air of the same diameter extending to the top of the atmosphere.

This simple device, called a **barometer,** works like a balance, one arm of which is loaded with the mass of mercury in the tube and the other with a column of air of the same cross-sectional area that extends to the top of the Earth's atmosphere, approximately 150 km above the surface of the earth. (see Fig. 9.2b). The height of the mercury column adjusts itself so that its mass and that of the air column become equal. This means that the two forces on the surface of the mercury in the dish are balanced. Day-to-day changes in the height of the column occur as the force exerted by the atmosphere varies with the weather. Atmospheric pressure varies strongly with altitude; it is lower at higher altitudes because the column of air pressing down is shorter and, therefore, has less mass.

How Torricelli's invention measures the pressure of the atmosphere is explained by Newton's second law of motion, which states:

$$\text{force} = \text{mass} \times \text{acceleration}$$

$$F = ma$$

in which the acceleration of a body (a) is the rate at which its velocity changes. The gravitational field of Earth exerts an attractive force that accelerates all bodies toward Earth. The standard acceleration due to the earth's gravitational field (usually denoted by g instead of a) is $g = 9.80665 \text{ m s}^{-2}$. Pressure is the force per unit area, or the total force, F, divided by the area, A:

$$P = \frac{F}{A} = \frac{mg}{A}$$

Because the volume of mercury in the barometer is $V = Ah$,

$$P = \frac{mg}{A} = \frac{mg}{V/h} = \frac{mgh}{V}$$

Writing the density as $\rho = m/V$ and substituting, we get

$$\boxed{P = \rho g h} \qquad [9.1]$$

We can use this equation to calculate the pressure exerted by the atmosphere. The density of mercury at 0°C, in SI units (see Appendix B for a description of SI units), is

$$\rho = 13.5951 \text{ g cm}^{-3} = 1.35951 \times 10^4 \text{ kg m}^{-3}$$

and the height of the mercury column under ordinary atmospheric conditions near sea level is close to 0.76 m (760 mm). Let's use exactly this value for the height in our computation:

$$\begin{aligned} P = \rho g h &= (1.35951 \times 10^4 \text{ kg m}^{-3})(9.80665 \text{ m s}^{-2})(0.760000 \text{ m}) \\ &= 1.01325 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2} \end{aligned}$$

Pressure is expressed in various units. The SI unit for pressure is the **pascal** (Pa), which is 1 kg m^{-1} s^{-2}. One **standard atmosphere** (1 atm) is defined as exactly 1.01325×10^5 Pa. The standard atmosphere is a useful unit because the pascal is inconveniently small and because "atmospheric pressure" is important as a standard of reference. We must express pressures in pascals when we perform calculations entirely in SI units.

For historical reasons, a number of different pressure units are commonly used in different fields of science and engineering. Although we will work primarily with the standard atmosphere, it is important that you recognize other units and be able to convert among them. For example, the atmospheric pressure (often called the barometric pressure) recorded in weather reports and forecasts is typically expressed as the height (in millimeters or inches) of the column of mercury it supports. One standard atmosphere supports a 760-mm column of mercury at

TABLE 9.2 Units of Pressure

Unit	Definition or Relationship
pascal (Pa)	1 kg m^{-1} s^{-2}
bar	1 × 10^5 Pa
atmosphere (atm)	101,325 Pa
torr	1/760 atm
760 mm Hg (at 0°C)	1 atm
14.6960 pounds per square inch (psi, lb in^{-2})	1 atm

0°C; thus, we often speak of 1 atm pressure as 760 mm or 30 inches (of mercury [Hg]). Because the density of mercury depends slightly on temperature, for accurate work it is necessary to specify the temperature and make the proper corrections to the density. A more precise term is the "torr," defined as 1 torr = 1/760 atm (or 760 torr = 1 atm) at *any* temperature. Only at 0°C do the torr and the millimeters of mercury (mm Hg) coincide. These and other units of pressure are summarized in Table 9.2.

Robert Boyle, an English natural philosopher and theologian, studied the properties of confined gases in the 17th century. He noted that a gas tends to spring back to its original volume after being compressed or expanded. Such behavior resembles that of metal springs, which were being investigated by his collaborator Robert Hooke. Boyle published his experiments on the compression and expansion of air in the 1662 monograph titled "The Spring of the Air and Its Effects."

Boyle studied how the volume of a confined gas responded to changes in pressure while the temperature was held constant. Boyle worked with a simple piece of apparatus: a J-tube in which air was trapped at the closed end by a column of mercury (Fig. 9.3). If the difference in height, *h*, between the two mercury levels in such a tube is 0, then the pressure of the air in the closed part exactly balances

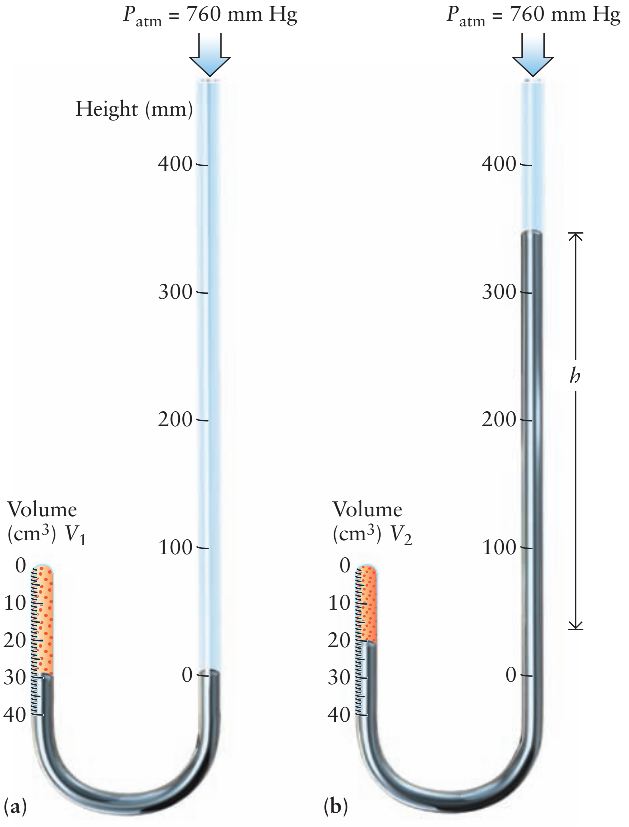

FIGURE 9.3 (a) Boyle's J-tube. When the heights of mercury on the two sides of the tube are the same, the pressure of the confined gas must equal that of the atmosphere, 1 atm or 760 mm Hg. (b) After mercury has been added, the pressure of the gas is increased by the number of millimeters of mercury in the height difference *h*. The compression of the gas causes it to occupy a smaller volume.

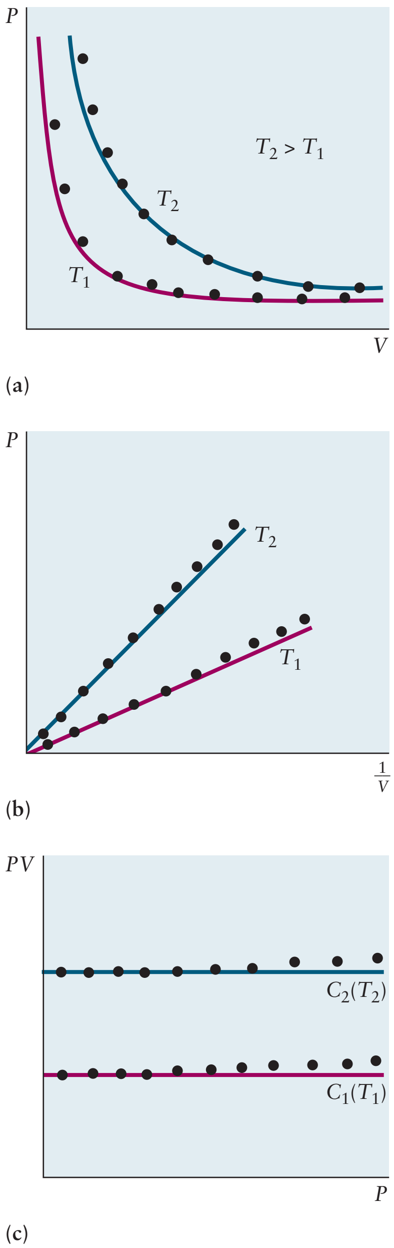

FIGURE 9.4 (a–c) Three ways of depicting Boyle's law. Small deviations from the law (especially apparent b and c) arise for real gases at higher pressures or smaller volumes.

that of the atmosphere; its pressure, P is 1 atm. Adding mercury to the open end of the tube increases the pressure applied to the confined air; its internal pressure increases by 1 mm Hg for every 1-mm difference between the levels of mercury on the open and closed sides of the tube. Expressed in atmospheres, the pressure in the closed end of the tube is

$$P = 1 \text{ atm} + \frac{h \text{ (mm)}}{760 \text{ mm atm}^{-1}}$$

The volume of the confined air can be read from the scale on the previously calibrated tube. The temperature is held constant by the ambient surroundings of the tube. Boyle discovered that the product of pressure and volume, PV, has the constant value C so long as temperature and the number of moles of confined gas remain fixed. The value of the constant C depends on the amount of gas and the temperature of the gas.

Boyle's data showed that P and V are inversely related, and *suggested* the relationship might be described by the equation $PV = C$, as shown in Figure 9.4a. Before the advent of graphing calculators and computers, it was not always easy to determine the mathematical function that best fit experimental data. With a limited amount of data, it is difficult to distinguish $P = C/V$ from $P = P^* \exp(-C/V)$, where P^* is some fixed reference value of pressure. How are we to know whether Boyle's experiments are best described by $PV = C$ or some more complicated equation? There are two ways of plotting the data to answer this question. The first is to rewrite Boyle's proposed equation in the form

$$P = \frac{C}{V} = C\left(\frac{1}{V}\right)$$

which makes P directly or linearly proportional to $1/V$. If Boyle's equation correctly fits his data, then replotting the data in the form P against $1/V$ (rather than V) should give a straight line passing through the origin with slope C (this is shown to be true in Figure 9.4b). Alternatively, if $PV = C$ is correct, replotting the data in the form PV against P should give a straight line independent of P (the results are shown in Figure 9.4c). Rewriting proposed equations to make them linear ($y = mx + b$) and plotting the data together with a proposed equation provides a good test of that equation's validity. The two plots studied here show convincingly that Boyle's equation accurately describes the relation between pressure and volume, at least over the range of temperatures and pressures measured.

$$PV = C \qquad \text{(fixed temperature and fixed amount of gas)} \qquad [9.2]$$

This result is known as **Boyle's law.**

Keep in mind that the constant C depends on the temperature T and the amount (number of moles n) of gas in the closed container. For each combination of T and n, the limiting value of C at low P can be obtained by extrapolating plots (such as Fig. 9.4c) to zero pressure. For 1 mol gas (for example, 31.999 g O_2, 28.013 g N_2, or 2.0159 g H_2) at 0°C, extrapolation of PV to zero pressure (as shown by the red line in Fig. 9.4c) gives a limiting value of 22.414 L atm for C. Therefore, for these conditions, Boyle's law takes the special form:

$$PV = 22.414 \text{ L atm} \qquad \text{(for 1 mol gas at 0°C)} \qquad [9.3]$$

If the pressure is 1.00 atm, the volume is 22.4 L; if P is 4.00 atm, V is 22.414/4.00 = 5.60 L.

Boyle's law is an idealized expression that is satisfied exactly by all gases at *very* low pressures. For real gases near 1 atm pressure, small corrections may be necessary for highly accurate studies of P-V-T behavior. At pressures beyond 50–100 atm, substantial corrections are necessary.

EXAMPLE 9.1

The long cylinder of a bicycle pump has a volume of 1131 cm^3 and is filled with air at a pressure of 1.02 atm. The outlet valve is sealed shut and the pump handle is pushed down until the volume of the air is 517 cm^3. Compute the pressure inside the pump. Express its value in atmospheres and pounds per square inch.

SOLUTION

Note that the temperature and amount of gas are not stated in this problem; thus, the value of 22.414 L atm cannot be used for the constant C. It is necessary only to assume that the temperature does not change as the pump handle is pushed down. If P_1 and P_2 are the initial and final pressures and V_1 and V_2 the initial and final volumes, then

$$P_1V_1 = P_2V_2$$

because the temperature and amount of air in the pump do not change. Substitution gives

$$(1.02 \text{ atm})(1131 \text{ cm}^3) = P_2(517 \text{ cm}^3)$$

which can be solved for P_2:

$$P_2 = 2.23 \text{ atm}$$

In pounds per square inch (see Table 9.2), this pressure is

$$P_2 = 2.23 \text{ atm} \times 14.696 \text{ psi atm}^{-1} = 32.8 \text{ psi}$$

Related Problems: 11, 12

Temperature and Charles's Law

Temperature is one of those elusive properties that we all think we understand but is, in fact, difficult to pin down in a quantitative fashion. We have an instinctive feeling (through the sense of touch) for *hot* and *cold*. Water at its freezing point is obviously colder than at its boiling point so we assign it a lower temperature. Both the Celsius and Fahrenheit temperature scales were defined using the freezing and boiling points of water. Water freezes at 0°C (32°F) and boils at 100°C (212°F). Although both scales use the same reference points, it is interesting to see how the size of the degree was defined and the reference temperatures were determined. Fahrenheit initially chose as reference points the freezing point for a saturated saltwater solution, which he assigned as 0° (then thought to be as cold as possible), and normal body temperature (that of his wife) assigned to be 96°. His choice of 96° for body temperature is thought to have been stimulated by the earlier work of Newton, who had devised a similar scale by dividing the interval between the boiling and freezing points of water into 12 units. As Fahrenheit's thermometers got better, he increased their resolution by several factors of 2 until the number 96 was reached. Further calibration led to the modern definition based on the freezing and boiling points of pure water cited earlier. The Celsius scale (originally called the centigrade scale) is a bit more logical. Celsius chose the same end points but divided the range into 100 units for ease of calculation.

Assigning two fixed points in this way does not show how to define a temperature scale. Ether boils at atmospheric pressure somewhere between 0°C and 100°C, but what temperature should be assigned to its boiling point? Further arbitrary choices are certainly not the answer. The problem is that temperature is not a mechanical quantity like pressure; therefore, it is more difficult to define.

One way around this problem is to find some mechanical property that depends on temperature and use it to define a temperature scale. If we measure the value of this property of an object immersed in boiling water and again when it is immersed in boiling ether, we can quantitatively compare the boiling points of these two liquids. A number of mechanical properties depend on temperature. For example, as liquid mercury is heated from 0°C to 100°C, its volume increases by 1.82%. This change in volume could be used to define a temperature scale. If we *assume* that the volume of mercury is a linear function of temperature, then we can simply measure temperature by measuring the volume of mercury in a tube (a mercury thermometer). The problem is that this definition is tied to the properties of a single substance, mercury, and rests on the assumption that the volume of a sample of mercury is directly proportional to the temperature. Can we define a temperature scale that is more universal, one that does not depend on the properties of a specific material or the assumption of linearity? To answer this question, let's examine the behavior of gases upon heating or cooling.

Boyle observed that the product of the pressure and volume of a confined gas changes on heating, but the first quantitative experiments on the temperature dependence of the properties of gases were performed by the French scientist Jacques Charles more than a century later. Charles observed that *all* gases expand by the same relative amount between the same initial and final temperatures, when studied at sufficiently low pressures. For example, heating a sample of N_2 from the freezing point of water to the boiling point causes the gas to expand to 1.366 times its original volume (Fig. 9.5). The same 36.6% increase in volume occurs for O_2, CO_2, and other gases. (In contrast, liquids and solids vary widely in their thermal expansion.) This universal behavior suggests that temperature is a linear function of gas volume. We write this function as

$$t = c\left(\frac{V}{V_0} - 1\right)$$

where V is the volume of the gas at temperature t, V_0 is its volume at the freezing point of water, and c is a constant that is the same for all gases. We have written the linear equation in this form to ensure that the freezing point of water (when $V = V_0$) will be at $t = 0$, corresponding to the zero of the Celsius scale of temperature. From the measured fractional increase in V to the boiling point (taken to be 100°C), the value of c can be determined. In 1802, Gay-Lussac reported a value for c of 267°C. Subsequent experiments have refined this result to give $c = 273.15°\text{C}$. The definition of temperature (in degrees Celsius) is then

$$t = 273.15°\text{C}\left(\frac{V}{V_0} - 1\right)$$

The temperature of a gas sample at low pressure can be measured by comparing its volume with the volume it occupies at the freezing point of water. For many

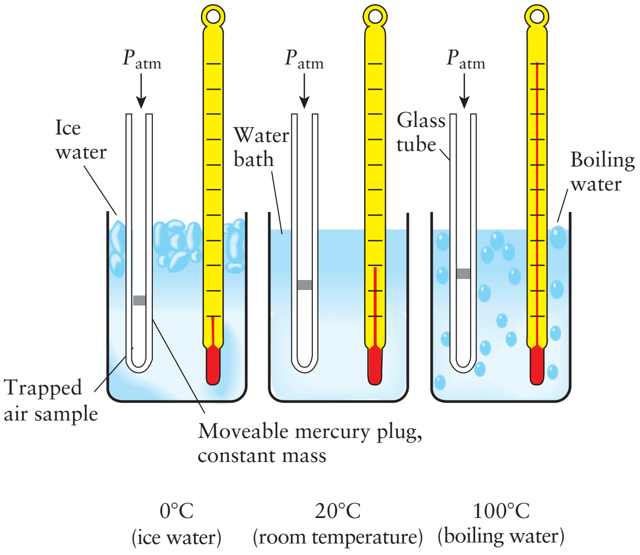

FIGURE 9.5 The volume of a gas confined at constant pressure increases as the temperature increases.

gases, atmospheric pressure is sufficiently low; but for highly accurate temperature determinations, it is necessary to use pressures below atmospheric or to apply small corrections.

With this definition of temperature in mind, let's return to mercury and measure its *actual* changes in volume with temperature. The result found is almost, but not quite, linear. If a mercury thermometer is calibrated to match the gas thermometer at 0°C and 100°C and if the scale in between is divided evenly into 100 parts to mark off degrees, a small error will result from using this thermometer. A temperature of 40.00°C on the gas thermometer will be read as 40.11°C on the mercury thermometer, because the volume of liquid mercury is not exactly a linear function of temperature.

We can rewrite the preceding equation to express the gas volume in terms of the temperature. The result is

$$V = V_0\left(1 + \frac{t}{273.15°\text{C}}\right) \qquad [9.4]$$

In words, the volume of a gas varies linearly with its temperature. This is the most common statement of **Charles's law,** but it is somewhat misleading because the linearity is built in through the definition of temperature. The key observation is the universal nature of the constant 273.15°C, which is the same for all gases at low pressures. Written in this form, Charles's law suggests that an interesting lower limit to the temperature exists. Negative temperatures on the Celsius scale correspond to temperatures below the freezing point of water and, of course, are meaningful. But what would happen as t approached -273.15°C? The volume would then approach zero (Fig. 9.6), and if t could go below this value, the volume would become negative, clearly an impossible result. We therefore surmise that $t = -273.15$°C is a fundamental limit below which the temperature cannot be lowered. All real gases condense to liquid or solid form before they reach this **absolute zero** of temperature, so we cannot check for the existence of this limit simply by measuring the volume of gases. More rigorous arguments show that *no* substance (gas, liquid, or solid) can be cooled below −273.15°C. In fact, it becomes increasingly difficult to cool a substance as absolute zero is approached. The coldest temperatures reached to date are less than 1 nanodegree above absolute zero.

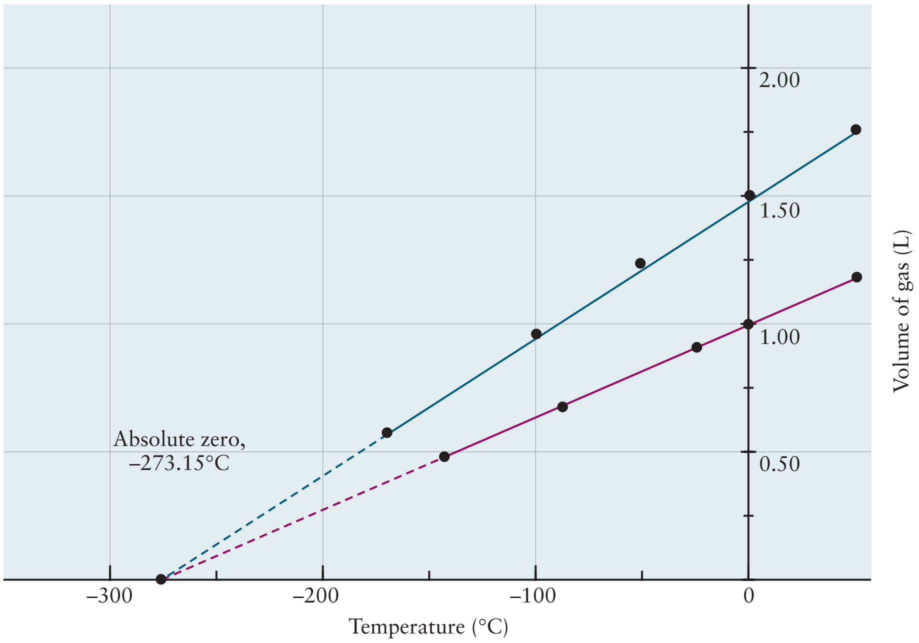

FIGURE 9.6 The volume of a sample of a gas is a function of temperature at constant pressure. The observed straight-line response of volume to temperature illustrates Charles's law. The volume of a particular sample of a gas (red line) is 1.0 L at a temperature of 0°C. Another sample of a gas (blue line) held at the same pressure takes up more volume at 0°C but shrinks faster as cooled. The *percentage* change in volume is the same as that of the first sample for every degree of temperature change. Extrapolation of the trends (dashed lines) predicts that the volumes of the samples go to zero at a temperature of −273.15°C. Similar observations are made regardless of the chemical identities of the gases.

The absolute zero of temperature is a compellingly logical choice as the zero point of a temperature scale. The easiest way to create such a new scale is to add 273.15 to the Celsius temperature, which leads to the **Kelvin temperature scale:**

$$T\text{ (Kelvin)} = 273.15 + t\text{ (Celsius)} \qquad [9.5]$$

The capital T signifies that this is an absolute scale, the unit of which is *kelvin* (K). Thus, a temperature of 25.00°C corresponds to 273.15 + 25.00 = 298.15 K. (**Note:** The unit is the kelvin, not the °K.) On this scale, Charles's law takes the following form:

$$V \propto T \qquad \text{(fixed temperature and fixed amount of gas)} \qquad [9.6]$$

where the proportionality constant is determined by the pressure and the amount (number of moles) of gas present. The ratios of volumes occupied at two different temperatures by a fixed amount of gas at fixed pressure are:

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$

EXAMPLE 9.2

A scientist studying the properties of hydrogen at low temperature takes a volume of 2.50 L hydrogen at atmospheric pressure and a temperature of 25.00°C and cools the gas at constant pressure to −200.00°C. Predict the volume that the hydrogen occupies at the lower temperature.

SOLUTION

The first step is always to convert temperatures to kelvins:

$$t_1 = 25.00°\text{C} \Rightarrow T_1 = 273.15 + 25.00 = 298.15\text{ K}$$

$$t_2 = -200.00°\text{C} \Rightarrow T_2 = 273.15 - 200.00 = 73.15\text{ K}$$

The ratio in Charles's law is

$$\frac{V_1}{T_1} = \frac{2.50\text{ L}}{298.15\text{ K}} = \frac{V_2}{T_2} = \frac{V_2}{73.15\text{ K}}$$

$$V_2 = \frac{(73.15\text{ K})(2.50\text{ L})}{298.15\text{ K}} = 0.613\text{ L}$$

Related Problems: 13, 14, 15, 16, 17, 18

9.3 The Ideal Gas Law

So far, we have empirically deduced several relationships between properties of gases. From Boyle's law,

$$V \propto \frac{1}{P} \qquad \text{(at constant temperature, fixed amount of gas)}$$

and from Charles's law,

$$V \propto T \qquad \text{(at constant pressure, fixed amount of gas)}$$

where T is the absolute temperature in kelvins. From Avogadro's hypothesis (Section 1.3) that equal volumes of different gases held at the same T and P contain equal numbers of particles,

$$V \propto n \qquad \text{(at constant temperature and pressure)}$$

where n is the number of moles of substance. These three statements may be combined in the form

$$V \propto \frac{nT}{P}$$

A proportionality constant called R converts this proportionality to an equation:

$$V = R\frac{nT}{P} \quad \text{or} \quad PV = nRT \qquad [9.7]$$

Because Avogadro's hypothesis states that equal volumes of all gases contain the same number of molecules (or moles), R is a *universal* constant. Equation 9.7 states the **ideal gas law,** which holds approximately for all gases near atmospheric pressure and room temperature and becomes increasingly accurate at lower pressure and higher temperature. It is a limiting law that describes the behavior of gases at low *densities*. We obtained the ideal gas law empirically from experimental studies of the P-V-T behavior of gases, and we shall see in Section 9.5 that the same relation is predicted by a molecular model of gases. The ideal gas law is our first example of a direct connection between the experimentally observed macroscopic behavior of matter and the structure and interactions of its constituent molecules.

Situations frequently arise in which a gas undergoes a change that takes it from some initial condition (described by P_1, V_1, T_1, and n_1) to a final condition (described by P_2, V_2, T_2, and n_2). Because R is a constant,

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} \qquad [9.8]$$

This is a useful alternative form of the ideal gas law.

EXAMPLE 9.3

A weather balloon filled with helium (He) has a volume of 1.0×10^4 L at 1.00 atm and 30°C. It rises to an altitude at which the pressure is 0.60 atm and the temperature is −20°C. What is the volume of the balloon then? Assume that the balloon stretches in such a way that the pressure inside stays close to the pressure outside.

SOLUTION

Because the amount of helium does not change, we can set n_1 equal to n_2 and cancel it out of Equation 9.8, giving

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Solving this for the only unknown quantity, V_2, gives

$$\begin{aligned} V_2 &= V_1\left(\frac{P_1T_2}{P_2T_1}\right) \\ &= 1.0 \times 10^4\ \text{L}\left(\frac{1.00\ \text{atm}}{0.60\ \text{atm}}\right)\left(\frac{253\ \text{K}}{303\ \text{K}}\right) \\ &= 1.4 \times 10^4\ \text{L} = 14{,}000\ \text{L} \end{aligned}$$

Remember that temperatures must always be converted to kelvins when using the ideal gas law.

Related Problems: 19, 20, 21, 22


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FIGURE 9.7 In a hot-air balloon, the volume remains nearly constant (the balloon is rigid) and the pressure is nearly constant as well (unless the balloon rises very high). Thus, *n* is inversely proportional to *T*; as the air inside the balloon is heated, its amount decreases and its density falls. This reduced density gives the balloon its lift.

The approach outlined in Example 9.3 can be applied when other combinations of the four variables (P, V, T, and n) remain constant (Fig. 9.7). When n and T remain constant, they can be canceled from the equation to give Boyle's law, which was used in solving Example 9.1. When n and P remain constant, this relation reduces to Charles's law, used in Example 9.2.

The numerical value of R depends on the units chosen for P and V. At the freezing point of water ($T = 273.15$ K) the product PV for 1 mol of any gas approaches the value 22.414 L atm at low pressures; hence, R has the value

$$R = \frac{PV}{nT} = \frac{22.414 \text{ L atm}}{(1.000 \text{ mol})(273.15 \text{ K})} = 0.082058 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

If P is measured in SI units of pascals (kg m^{-1} s^{-2}) and V in cubic meters, then R has the value

$$R = \frac{(1.01325 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2})(22.414 \times 10^{-3} \text{ m}^3)}{(1.0000 \text{ mol})(273.15 \text{ K})}$$

$$= 8.3145 \text{ kg m}^2\ s^{-2} \text{ mol}^{-1} \text{ K}^{-1}$$

Because 1 kg m^2 s^{-2} is defined to be 1 *joule* (the SI unit of energy, abbreviated J), the gas constant may also be expressed as

$$R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$$

EXAMPLE 9.4

What mass of helium is needed to fill the weather balloon from Example 9.3?

SOLUTION

First, solve the ideal gas law for n:

$$n = \frac{PV}{RT}$$

If P is expressed in atmospheres and V is expressed in liters, then the value $R = 0.08206$ L atm mol^{-1} K^{-1} must be used.

$$n = \frac{(1.00 \text{ atm})(1.00 \times 10^4 \text{ L})}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(303.15 \text{ K})} = 402 \text{ mol}$$

Because the molar mass of helium is 4.00 g mol^{-1}, the mass of helium required is

$$(402 \text{ mol})(4.00 \text{ g mol}^{-1}) = 1610 \text{ g} = 1.61 \text{ kg}$$

Related Problems: 23, 24

Chemical Calculations for Gases

One of the most important applications of the gas laws in chemistry is to calculate the volumes of gases consumed or produced in chemical reactions. If the conditions of pressure and temperature are known, the ideal gas law can be used to convert between the number of moles and gas volume. Instead of working with the mass of each gas taking part in the reaction, we can then use its volume, which is easier to measure. This is illustrated by the following example.

EXAMPLE 9.5

Concentrated nitric acid acts on copper to give nitrogen dioxide and dissolved copper ions (Fig. 9.8) according to the balanced chemical equation

$$\text{Cu}(s) + 4\ \text{H}^+(aq) + 2\ \text{NO}_3^-(aq) \longrightarrow 2\ \text{NO}_2(g) + \text{Cu}^{2+}(aq) + 2\ \text{H}_2\text{O}(\ell)$$


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FIGURE 9.8 When copper metal is immersed in concentrated nitric acid, the copper is oxidized and an aqueous solution of blue copper(II) nitrate forms. In addition, some of the nitrate ion is reduced to brown gaseous nitrogen dioxide, which bubbles off.

Suppose that 6.80 g copper is consumed in this reaction, and that the NO_2 is collected at a pressure of 0.970 atm and a temperature of 45°C. Calculate the volume of NO_2 produced.

SOLUTION

The first step (as in Fig. 2.4) is to convert from the mass of the known reactant or product (in this case, 6.80 g Cu) to number of moles by using the molar mass of copper, 63.55 g mol^{-1}:

$$\frac{6.80 \text{ g Cu}}{63.55 \text{ g mol}^{-1}} = 0.107 \text{ mol Cu}$$

Next, the number of moles of NO_2 generated in the reaction is calculated using the stoichiometric coefficients in the balanced equation:

$$0.107 \text{ mol Cu} \times \left(\frac{2 \text{ mol NO}_2}{1 \text{ mol Cu}}\right) = 0.214 \text{ mol NO}_2$$

Finally, the ideal gas law is used to find the volume from the number of moles (remember that the temperature must first be expressed in kelvins by adding 273.15):

$$V = \frac{nRT}{P} = \frac{(0.214 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(273.15 + 45)\text{K}}{0.970 \text{ atm}} = 5.76 \text{ L}$$

Therefore, 5.76 L NO_2 is produced under these conditions.

Related Problems: 25, 26, 27, 28, 29, 30, 31, 32

9.4 Mixtures of Gases

Suppose a mixture of gases occupies a container at a certain temperature. How does each gas contribute to the total pressure of the mixture? We define the **partial pressure** of each gas as the pressure that gas would exert if it alone were present in the container. John Dalton concluded, from experiment, that the total pressure measured, P_{tot}, is the sum of the partial pressures of the individual gases (Fig. 9.9). This should come as no surprise given the validity of Avogadro's hypothesis. Even so, it is an important result. **Dalton's Law** holds under the same conditions as the ideal gas law itself: It is approximate at moderate pressures and becomes increasingly more accurate as the pressure is lowered.

For a gas mixture at low pressure, the partial pressure of one component, A, is

$$P_A = n_A \frac{RT}{V}$$

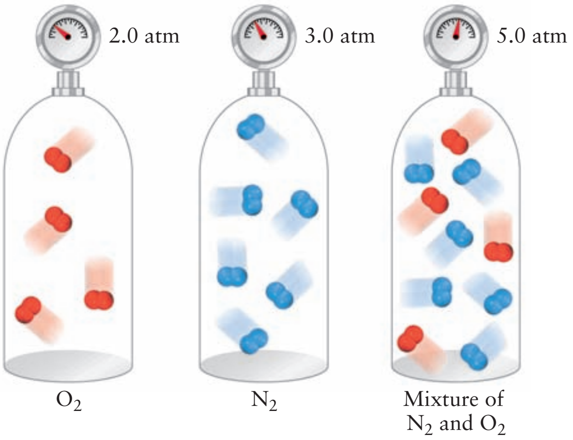


FIGURE 9.9 According to Dalton's law, the total pressure of a gas mixture is the sum of the pressures exerted by the individual gases. Note that the total volume is the same in all three containers.

The total pressure is the sum of the partial pressures:

$$P_{\text{tot}} = P_{\text{A}} + P_{\text{B}} + P_{\text{C}} + \cdots = (n_{\text{A}} + n_{\text{B}} + n_{\text{C}} + \cdots)\frac{RT}{V} = n_{\text{tot}}\frac{RT}{V} \qquad [9.9]$$

where n_{tot} is the total number of moles in the gas mixture. Dividing the first equation by the second gives

$$\frac{P_{\text{A}}}{P_{\text{tot}}} = \frac{n_{\text{A}}}{n_{\text{tot}}} \quad \text{or} \quad P_{\text{A}} = \frac{n_{\text{A}}}{n_{\text{tot}}}P_{\text{tot}}$$

We define

$$X_{\text{A}} = \frac{n_{\text{A}}}{n_{\text{tot}}}$$

as the **mole fraction** of A in the mixture—that is, the number of moles of A divided by the total number of moles present. Then

$$P_{\text{A}} = X_{\text{A}}P_{\text{tot}} \qquad [9.10]$$

The partial pressure of any component in a mixture of ideal gases is the total pressure multiplied by the mole fraction of that component. Note that the volume fractions in Table 9.1 are the same as mole fractions.

EXAMPLE 9.6

When NO_2 is cooled to room temperature, some of it reacts to form a *dimer,* N_2O_4, through the reaction

$$2\ NO_2(g) \longrightarrow N_2O_4(g)$$

Suppose 15.2 g of NO_2 is placed in a 10.0-L flask at high temperature and the flask is cooled to 25°C. The total pressure is measured to be 0.500 atm. What partial pressures and mole fractions of NO_2 and N_2O_4 are present?

SOLUTION

Initially, there is 15.2 g/46.01 g mol^{-1} = 0.330 mol NO_2, and therefore, the same number of moles of nitrogen atoms. If at 25°C there are n_{NO_2} moles NO_2 and $n_{N_2O_4}$ moles N_2O_4, then, because the total number of moles of nitrogen atoms is unchanged,

$$n_{NO_2} + 2n_{N_2O_4} = 0.330\text{ mol} \qquad \text{(a)}$$

To find a second relation between n_{NO_2} and $n_{N_2O_4}$, use Dalton's law:

$$P_{NO_2} + P_{N_2O_4} = 0.500\text{ atm}$$

$$\frac{RT}{V}n_{NO_2} + \frac{RT}{V}n_{N_2O_4} = 0.500\text{ atm}$$

$$n_{NO_2} + n_{N_2O_4} = 0.500\text{ atm}\,\frac{V}{RT}$$

$$= \frac{(0.500\text{ atm})(10.0\text{ L})}{(0.08206\text{ L atm mol}^{-1}\text{ K}^{-1})(298\text{ K})}$$

$$n_{NO_2} + n_{N_2O_4} = 0.204\text{ mol} \qquad \text{(b)}$$

Subtracting Equation b from Equation a gives

$$n_{N_2O_4} = 0.126 \text{ mol}$$

$$n_{NO_2} = 0.078 \text{ mol}$$

From these results, NO_2 has a mole fraction of 0.38 and a partial pressure of (0.38)(0.500 atm) = 0.19 atm, and N_2O_4 has a mole fraction of 0.62 and a partial pressure of (0.62)(0.500 atm) = 0.31 atm.

Related Problems: 33, 34, 35, 36, 37, 38

9.5 The Kinetic Theory of Gases

The ideal gas law summarizes certain physical properties of gases at low pressures. It is an empirical law, the consequence of experimental observations, but its simplicity and generality prompt us to ask whether it has some underlying microscopic explanation that involves the properties of atoms and molecules in a gas. Such an explanation would allow other properties of gases at low pressures to be predicted and would clarify why real gases deviate from the ideal gas law to small but measurable extents. Such a theory was developed in the 19th century, notably by the physicists Rudolf Clausius, James Clerk Maxwell, and Ludwig Boltzmann. The **kinetic theory of gases** is one of the great milestones of science, and its success provides strong evidence for the atomic theory of matter (see discussion in Chapter 1).

This section introduces a type of reasoning different from that used so far. Instead of proceeding from experimental observations to empirical laws, we begin with a model and use the basic laws of physics with mathematical reasoning to show how this model helps explain the measured properties of gases. In this way, the kinetic theory of gases provides a microscopic understanding of Boyle's law and also a microscopic mechanical definition of temperature as a measure of the average kinetic energy of the molecules in a gas.

The underlying assumptions of the kinetic theory of gases are simple:

1. A pure gas consists of a large number of identical molecules separated by distances that are great compared with their size.
2. The gas molecules are constantly moving in random directions with a distribution of speeds.
3. The molecules exert no forces on one another between collisions, so between collisions they move in straight lines with constant velocities.
4. The collisions of molecules with the walls of the container are *elastic;* no energy is lost during a collision.

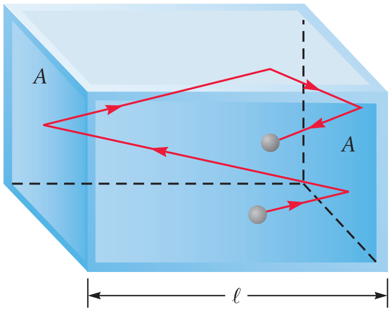


FIGURE 9.10 The path of a molecule in a box.

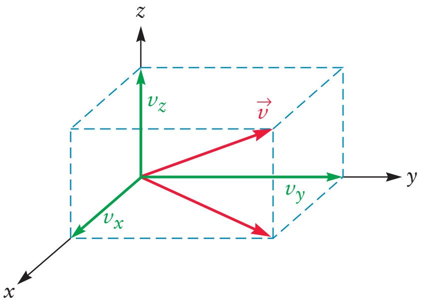


FIGURE 9.11 Velocity is shown by an arrow of length *v.* It can be separated into three components, v_x, v_y, and v_z, along the three Cartesian coordinate axes and projected into the *x-y* plane.

The Meaning of Temperature

We first use the kinetic theory of gases to find a relation among pressure, volume, and the motions of molecules in an ideal gas. Comparing the result obtained with the ideal gas law ($PV = nRT$) provides a deeper understanding of the meaning of temperature.

Suppose a container has the shape of a rectangular box of length ℓ, with end faces, each of which has area A (Fig. 9.10). A single molecule moving with speed u in some direction is placed in the box. It is important to distinguish between **speed** and **velocity.** The velocity of a molecule specifies both the rate at which it is moving (its speed, in meters per second) and the direction of motion. As shown in Figure 9.11, the velocity can be indicated by an arrow (vector) $\vec{v}$, which has a length

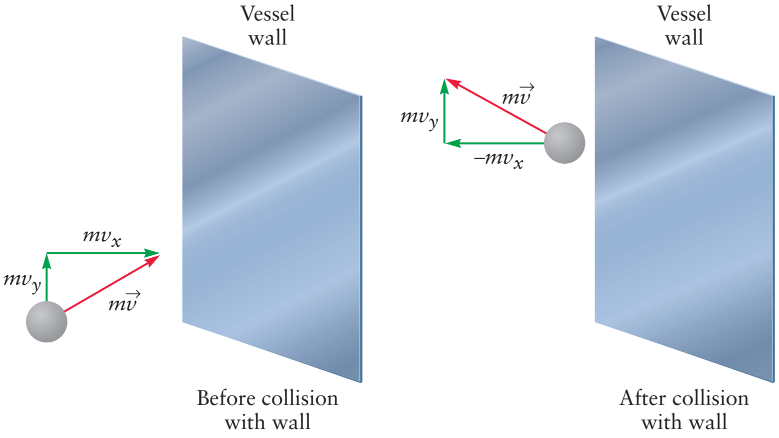


FIGURE 9.12 An elastic collision of a molecule with a wall. The component of the molecule's momentum perpendicular to the wall reverses sign, from mv_x to $-mv_x$. The component parallel to the wall, mv_y, is unchanged. The total momentum is shown by the red arrow. Although the direction of the red arrow is changed by the collision, its length, which represents the magnitude of the momentum, is not changed. Speeds of molecules are not affected by elastic collisions with the walls of the container.

equal to the speed u and which points in the direction of motion of the molecule. The velocity can also be represented by its components along three coordinate axes: v_x, v_y, and v_z. These are related to the speed, u, by the Pythagorean theorem:

$$u^2 = v_x^2 + v_y^2 + v_z^2$$

The **momentum** of a molecule, $\vec{p}$, is its velocity multiplied by its mass. When the molecule collides elastically with a wall of the box, such as one of the end faces of area A, the y and z components of the velocity, v_y and v_z, are unchanged, but the x component (perpendicular to A) reverses sign (Fig. 9.12). The change in the x component of the momentum of the molecule, $\Delta p_{x,\text{mol}}$, is

$$\Delta p_{x,\text{mol}} = \text{final momentum} - \text{initial momentum} = m(-v_x) - mv_x = -2\,mv_x$$

The total momentum of the system (molecule plus box) must be conserved, so this momentum change of the molecule is balanced by an equal and opposite momentum change given to the wall:

$$\Delta p_{x,\text{wall}} = 2mv_x$$

After colliding with the wall, the molecule reverses direction, strikes the opposite face of the box, and then again approaches the original face. In between, it may strike the top, bottom, and sides. These collisions do not change v_x, so they do not affect the time between collisions with the original end face (see Fig. 9.10). The distance traveled in the x direction is 2ℓ, and the magnitude of the velocity component in this direction is v_x, so the time elapsed between collisions with this end face is

$$\Delta t = \frac{2\ell}{v_x}$$

The momentum transferred to the wall per second is the momentum change per collision divided by Δt:

$$\frac{\Delta p_{x,\text{wall}}}{\Delta t} = \frac{2mv_x}{2\ell/v_x} = \frac{mv_x^2}{\ell}$$

From Newton's second law, the force exerted on the original face by repeated collisions of this molecule is:

$$f = ma = m\frac{\Delta v}{\Delta t} = \frac{\Delta p}{\Delta t} = \frac{mv_x^2}{\ell}$$

Suppose now that a large number, N, of molecules of mass m are moving independently in the box with x components of velocity, v_{x1}, v_{x2}, v_{x3}, and so forth. Then the total force exerted on the face by the N molecules is the sum of the forces exerted by the individual molecules:

$$F = \frac{mv_{x1}^2}{\ell} + \frac{mv_{x2}^2}{\ell} + \cdots + \frac{mv_{xN}^2}{\ell} = \frac{Nm}{\ell}\,\overline{v_x^2}$$

where

$$\overline{v_x^2} = \frac{1}{N}\,(v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2)$$

Here, $\overline{v_x^2}$ is the average of the square of the x component of the velocity of the N molecules, obtained by summing v_x^2 for the N molecules and dividing by N. The pressure is the total force on the wall divided by the area, A, so

$$P = \frac{F}{A} = \frac{Nm}{A\ell}\,\overline{v_x^2}$$

Because $A\ell$ is the volume, V, of the box, we conclude that

$$PV = Nm\overline{v_x^2}$$

There is no preferred direction of motion for the gas molecules; thus, $\overline{v_x^2}$, $\overline{v_y^2}$, and $\overline{v_z^2}$ should all be equal to one other. We therefore conclude that

$$\overline{u^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}$$

so

$$PV = \tfrac{1}{3}\,Nm\overline{u^2} \qquad [9.11]$$

where $\overline{u^2}$ is the **mean-square speed** of the gas molecules. From the ideal gas law,

$$PV = nRT$$

so, we conclude that

$$\tfrac{1}{3}\,Nm\overline{u^2} = nRT$$

We have achieved our major goal with the derivation of this equation: a relationship between the temperature and the speeds of molecules. It can be simplified to provide additional insights. The equation has the number of molecules, N, on the left and the number of moles, n, on the right. Because N is just n multiplied by Avogadro's number, N_A, we can divide both sides by n to find

$$\tfrac{1}{3}\,N_A m\overline{u^2} = RT \qquad [9.12]$$

Let's examine this equation in two ways. First, we note that the kinetic energy of a molecule of mass m moving at speed u is equal to $\frac{1}{2}\,mu^2$, so the *average* kinetic energy of N_A molecules (1 mol), which we denote by $\overline{E}$, is $\frac{1}{2}\,N_A m\overline{u^2}$. This quantity is exactly the same as that in the left side of Equation 9.12, with the factor $\frac{1}{2}$ replacing $\frac{1}{3}$:

$$\overline{E} = N_A m\overline{u^2} = \tfrac{3}{2} \times \left(\tfrac{1}{3}\,N_A m\overline{u^2}\right) = \tfrac{3}{2}\,RT \qquad [9.13]$$

We obtain the average kinetic energy per molecule, $\overline{\varepsilon}$, by dividing $\overline{E}$ by Avogadro's number:

$$\overline{\varepsilon} = \tfrac{3}{2}\,k_B T \qquad [9.14]$$

where k_B is **Boltzmann's constant** and is defined as R/N_A. The average kinetic energy of the molecules of a gas depends only on the temperature. It does not depend on the mass of the molecules or their number density in the gas. This relation is the most fundamental result of the kinetic theory of gases, and it is used in all branches of science.

A second way to look at the equation is to recall that if m is the mass of a single molecule, then $N_A m$ is the mass of 1 mol of molecules—the molar mass, abbreviated $\mathcal{M}$. Solving Equation 9.13 for the mean-square speed, we find that

$$\overline{u^2} = \frac{3RT}{\mathcal{M}} \qquad [9.15]$$

The mean-square speed of a gas molecule is proportional to temperature and inversely proportional to its mass. All molecules move faster at higher temperatures, and lighter molecules move faster than heavier ones at the same temperature.

Distribution of Molecular Speeds

One of the fundamental assumptions of the kinetic theory is that the molecules travel through the gas with a range of possible speeds. We would like to know how the molecules are distributed over the range of possible speeds.

As a first step, we can get some sense of the typical speeds in the gas by the following method. We define the **root-mean-square speed,** u_{rms}, as the square root of the mean-square speed $3RT/\mathcal{M}$:

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{\mathcal{M}}} \qquad [9.16]$$

This equation makes sense only when all of its terms are expressed in a self-consistent system of units such as the SI system. The appropriate value used for R is

$$R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} = 8.3145 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1}$$

Note that molar masses $\mathcal{M}$ must be converted to *kilograms* per mole for use in the equation. The final result is expressed in the SI unit of speed, meters per second.

EXAMPLE 9.7

Calculate u_{rms} for (**a**) a He atom, (**b**) an oxygen molecule, and (**c**) a xenon atom at 298 K.

SOLUTION

Because the factor $3RT$ appears in all three expressions for u_{rms}, let's calculate it first:

$$3RT = (3)(8.3145 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1})(298 \text{ K}) = 7.43 \times 10^3 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1}$$

The molar masses of He, O_2, and Xe are 4.00 g mol^{-1}, 32.00 g mol^{-1}, and 131.3 g mol^{-1}, respectively. Convert them to 4.00×10^{-3} kg mol^{-1}, 32.00×10^{-3} kg mol^{-1}, and 131.3×10^{-3} kg mol^{-1}, and insert them together with the value for $3RT$ into the equation for u_{rms}:

$$u_{\text{rms}}(\text{He}) = \sqrt{\frac{7.43 \times 10^3 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1}}{4.00 \times 10^{-3} \text{ kg mol}^{-1}}} = 1360 \text{ m s}^{-1}$$

$$u_{\text{rms}}(\text{O}_2) = \sqrt{\frac{7.43 \times 10^3 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1}}{32.00 \times 10^{-3} \text{ kg mol}^{-1}}} = 482 \text{ m s}^{-1}$$

$$u_{\text{rms}}(\text{Xe}) = \sqrt{\frac{7.43 \times 10^3 \text{ kg m}^2 \text{ s}^{-2} \text{ mol}^{-1}}{131.3 \times 10^{-3} \text{ kg mol}^{-1}}} = 238 \text{ m s}^{-1}$$

At the same temperature, the He, O_2, and Xe molecules all have the same average kinetic energy; lighter molecules move faster to compensate for their smaller masses. These rms speeds convert to 3050, 1080, and 532 mph, respectively. The average molecule moves along quite rapidly at room temperature!

Related Problems: 41, 42, 43, 44

It is useful to have a complete picture of the entire distribution of molecular speeds. This turns out to be important when we study chemical kinetics (see Chapter 18), where we will need to know what fraction of a sample of molecules has kinetic energy above the minimum necessary for a chemical reaction. In particular, we would like to know what fraction of molecules, $\Delta N/N$, have speeds between u and $u + \Delta u$. This fraction gives the speed distribution function $f(u)$:

$$\frac{\Delta N}{N} = f(u)\,\Delta u$$

The speed distribution of the molecules in a gas has been measured experimentally by an apparatus sketched in Figure 9.13. The entire apparatus is enclosed in a large vacuum chamber. The molecules leak out of their container to form a *molecular beam,* which passes into a speed analyzer. The analyzer consists of two rotating plates, each with a notch in its edge, separated by the fixed distance L. The plates are rotated so the notches align and permit molecules to pass through both to reach the detector only for a short time interval, $\Delta\tau$. Only those molecules with speeds in the range $\Delta u = L/\Delta\tau$ reach the detector and are counted. The entire speed distribution can be mapped out by progressively varying the duration of the measurement time interval, $\Delta\tau$.

The function $f(u)$ was predicted theoretically by Maxwell and Boltzmann about 60 years before it was first measured. It is called the **Maxwell–Boltzmann speed distribution** for a gas of molecules of mass m at temperature T and it has the following form:

$$f(u) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} u^2 \exp(-mu^2/2k_B T) \qquad [9.17]$$

where Boltzmann's constant k_B was defined in Equation 9.14. This distribution is plotted in Figure 9.14 for several temperatures. As the temperature is raised, the entire distribution of molecular speeds shifts toward higher values. Few molecules

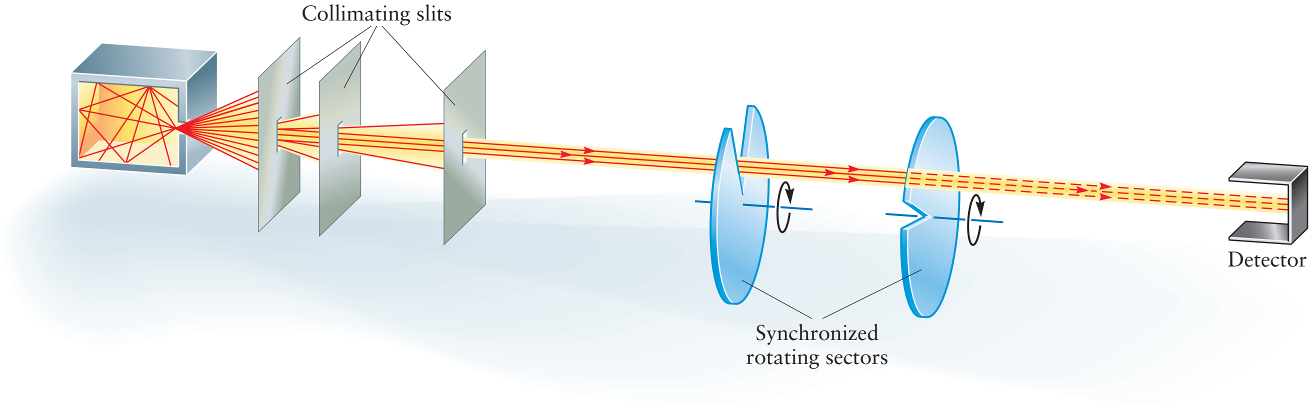


FIGURE 9.13 A device for measuring the distribution of molecular speeds. Only those molecules with the correct velocity to pass through *both* rotating sectors will reach the detector, where they will be counted. Changing the rate of rotation of the sectors allows the speed distribution to be determined.

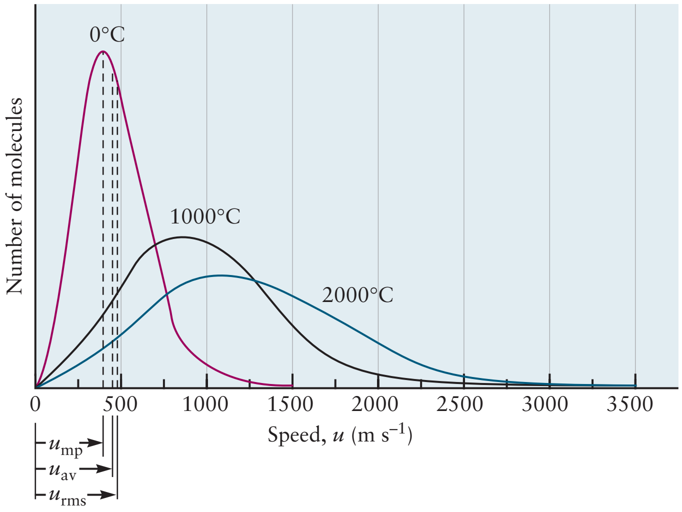


FIGURE 9.14 The Maxwell–Boltzmann distribution of molecular speeds in nitrogen at three temperatures. The peak in each curve gives the most probable speed, u_{mp}, which is slightly smaller than the root-mean-square speed, u_{rms}. The average speed u_{av} (obtained simply by adding the speeds and dividing by the number of molecules in the sample) lies in between. All three measures give comparable estimates of typical molecular speeds and show how these speeds increase with temperature.

have either very low or very high speeds; thus, $f(u)$ is small in these limits and has a maximum at some intermediate speed.

An alternative interpretation of the Maxwell-Boltzmann speed distribution is helpful in statistical analysis of the experiment. Experimentally, the probability that a molecule selected from the gas will have speed in the range Δu is defined as the fraction $\Delta N/N$ discussed earlier. Because $\Delta N/N$ is equal to $f(u)\,\Delta u$, we interpret this product as the probability predicted from theory that any molecule selected from the gas will have speed between u and $u + \Delta u$. In this way we think of the Maxwell-Boltzmann speed distribution $f(u)$ as a *probability distribution.* It is necessary to restrict Δu to very small ranges compared with u to make sure the probability distribution is a continuous function of u. An elementary introduction to probability distributions and their applications is given in Appendix C.6. We suggest you review that material now.

A probability distribution gives a quick visual indication of the likely outcome of the experiment it describes. The **most probable speed** u_{mp} is the speed at which $f(u)$ has its maximum. For the Maxwell–Boltzmann distribution function, this is

$$u_{mp} = \sqrt{\frac{2k_BT}{m}} = \sqrt{\frac{2RT}{\mathcal{M}}} \qquad [9.18]$$

A probability distribution enables us to calculate the average of the values obtained in several repetitions of the experiment it describes. The procedure is described in Appendix C.6. For the Maxwell–Boltzmann distribution, this calculation gives the **average speed** $\bar{u}$, which is

$$\bar{u} = \sqrt{\frac{8k_BT}{\pi m}} = \sqrt{\frac{8RT}{\pi \mathcal{M}}} \qquad [9.19]$$

If a probability distribution is symmetrical about its maximum, like the familiar "bell curve," the most probable value and the average value are the same. The Maxwell–Boltzmann distribution is not symmetrical; the area under the curve to the right of the maximum is somewhat larger than the area under the curve to the left of the maximum. (The next paragraphs use the mathematical form of the distribution to explain this fact.) Consequently, $\bar{u}$ will be larger than the most probable value of u.

The root-mean-square value can be calculated from the probability distribution, as shown in Appendix C.6. For a symmetrical distribution, this would be equal to the average value. For the Maxwell–Boltzmann distribution, we have already seen that

$$u_{\text{rms}} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3RT}{\pi\mathcal{M}}}$$

which verifies that $\overline{u} < u_{\text{rms}}$.

There are several possible ways to characterize a non-symmetrical probability distribution by a single number. The three different speeds discussed above serve this purpose for the Maxwell–Boltzmann distribution. Because the distribution is non-symmetrical, they are close to each other but are not equal. They stand in the ratio:

$$u_{\text{mp}}:\overline{u}:u_{\text{rms}} = 1.000:1.128:1.1225$$

It is not important for you to memorize these ratios. But you should understand that each quantity is a measure of the "average" speed of the molecules described by the distribution. Different applications require different choices among these quantities. You will learn how to make these connections in more advanced work.

The Maxwell–Boltzmann distribution is not symmetrical because it has the following mathematical form

$$f(u) \propto u^2 \exp(-mu^2/2k_BT)$$

which describes a competition between the two factors that depend on u^2. The competition arises because these factors behave oppositely, for physical reasons, as the value of u changes. We can get a great deal of physical insight into the distribution by studying the behavior of these factors separately while T is held constant.

The exponential factor can be viewed graphically as the right half of a bell curve with its maximum at $u = 0$ (Fig. 9.15). At low values of u, this factor behaves as $\exp(-mu^2/2k_BT) \longrightarrow \exp(-0) = 1$. At very large values of u, this factor behaves as $\exp(-mu^2/k_BT) = 1/[\exp(mu^2/k_BT)] \longrightarrow 1/\infty = 0$. The role of this factor is to describe the statistical weight given to each value of u in relation to T. The limits we have just examined shows this factor gives large statistical weight to small values of u, and increasingly small weight to large values of u, eventually forcing the distribution to fall off to zero at extremely high values of u. This is exactly what we expect on physical grounds.

The factor u^2 can be viewed as the right half of a parabola with its minimum at $u = 0$ (see Fig. 9.15). The value of this factor approaches zero as u decreases towards 0, and it grows without bound as u becomes extremely large. Although we do not provide all the details, the role of this factor is to count the number of different ways molecules in the gas can achieve a particular value of the speed, u. With Avogadro's number of molecules moving around the vessel, it is physically sensible that many different combinations of velocity vectors correspond to a

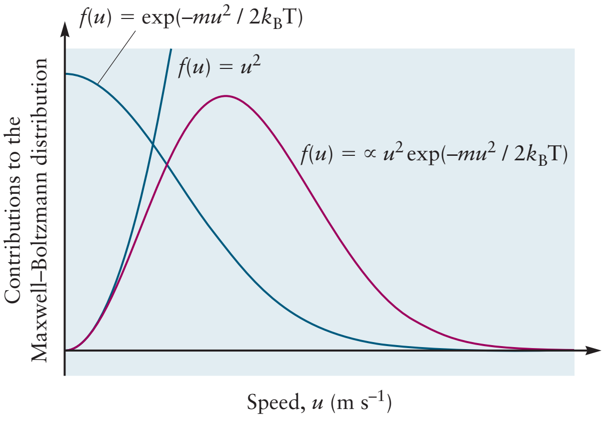


FIGURE 9.15 Mathematical form of the Maxwell–Boltzmann speed distribution. The factor u^2 cuts off the distribution at small values of *u*, whereas the exponential factor causes it to die off at large values of *u*. The competition between these effects causes the distribution to achieve its maximum value at intermediate values of *u*.

given value of the speed. And, we expect the number of such combinations to increase as the value of the speed increases. The shape of this factor strongly favors molecules with large values of u and it rapidly cuts off the distribution for small values of u.

The net result of these two competing factors is to keep the probability small for both extremely large and extremely small values of u. The probability will have a maximum at some intermediate value of u where the increasing effect of u^2 is just balanced by the decreasing effect of the exponential factor (see Fig. 9.15). This is the *most probable* value of u, denoted by u_{mp}, and it can be identified by setting to zero the derivative of the curve with respect to u. Because u^2 approaches zero for small values of u more rapidly than the exponential factor approaches zero for large values of u, the probability is larger to the right side of the maximum. The area under the curve to the right of the maximum is somewhat larger than the area under the curve to the left of the maximum. Consequently, the average value of u denoted by $\bar{u}$ will be larger than the most probable value of u. This is illustrated in Figure 9.14, which shows that $u_{\text{mp}} < \bar{u} < u_{\text{rms}}$.

The behavior of these competing factors also explains why the distribution becomes broader and its maximum moves to a higher value of u as the temperature increases (see Fig. 9.14). The maximum increases because the value of u at which the parabolic factor u^2 is cut off by the exponential factor increases as T increases. This happens because a particular value of u that would make $\exp(-mu^2/2k_{\text{B}}T) \ll 1$ at low T will now make $\exp(-mu^2/2k_{\text{B}}T) \longrightarrow \exp(-0) = 1$ at higher T. The distribution broadens because the falloff after the maximum is slower at high T than at low T. The reason is that as T increases, the value of u at which $\exp(-mu^2/2k_{\text{B}}T) \longrightarrow 0$ also increases. The net effect at higher T is that larger values of u become accessible, so the molecules are spread over a broader range of speeds.

The Maxwell–Boltzmann speed distribution defines temperature in the kinetic theory of gases as proportional to the average kinetic energy per molecule through Equation 9.14. Unless the molecular speed distribution for a given gas corresponds to the Maxwell–Boltzmann distribution, temperature has no meaning for the gas. Temperature describes a system of gaseous molecules only when their speed distribution is represented by the Maxwell–Boltzmann function. Consider a closed container filled with molecules whose speed distribution is not "Maxwellian." Such a situation is possible (for example, just after an explosion), but it cannot persist for long. Any distribution of molecular speeds other than a Maxwell–Boltzmann distribution quickly becomes Maxwellian through molecular collisions that exchange energy. Once attained, the Maxwell–Boltzmann distribution persists indefinitely (or at least until some new disturbance is applied). The gas molecules have come to **thermal equilibrium** with one another, and we can speak of a system as having a temperature only if the condition of thermal equilibrium exists.

A DEEPER LOOK

9.6 Distribution of Energy among Molecules

The kinetic molecular theory of gases relates the macroscopic properties of a gas to the structure of the constituent molecules, the forces between them, and their motions. Because the number of molecules in a sample of gas is so incredibly large—28 g nitrogen contains 6.02×10^{23} molecules—we give up the idea of following the detailed motions of any one molecule and rely on a statistical description that gives the *probability* of finding a molecule in the gas at a certain position, with a certain speed, with a certain value of energy, and so on. Treating the molecules as point masses obeying classical mechanics and using simple statistical arguments, the kinetic theory shows that the temperature of the gas is proportional to the average kinetic energy per molecule. This relation not only provides a microscopic interpretation of the concept of temperature, but it also indicates the typical values of molecular kinetic energy that occur in a gas at a particular temperature.

Now we want to determine the relation between temperature and the energy involved in other kinds of molecular motions that depend on molecular structure, not just the translation of the molecule. This relation is provided by the *Boltzmann energy distribution,* which relies on the quantum description of molecular motions. This section defines the Boltzmann distribution and uses it to describe the vibrational energy of diatomic molecules in a gas at temperature *T.*

The Boltzmann energy distribution is one of the most widely used relations in the natural sciences, because it provides a reliable way to interpret experimental results in terms of molecular behavior. You should become skilled in its applications.

The Boltzmann Energy Distribution

Just as in the previous section, we start with a model system in which gaseous molecules move around inside a container held at temperature *T.* The molecules collide with the container walls but not with one another. We can achieve this condition by setting up the experiment with sufficiently low pressure in the system. But this time we assume that the molecules have quantum states described by a quantum number n and represented on an energy level diagram where the energy of each state is labeled ε_n. After the system has settled down to equilibrium, how many of the molecules are in their ground state? To what extent are the excited states populated? The answers depend on the probability that a molecule in the gas is in the quantum state n, which is given by the **Boltzmann energy distribution:**

$$P(n) = C\exp(-\varepsilon_n/\mathrm{k_B}T) \qquad [9.20]$$

where C is a normalization factor and k_B is Boltzmann's constant. This equation was derived for classical systems by Ludwig Boltzmann even before quantum mechanics had been invented. Max Planck used a version of the Boltzmann distribution in formulating his theory of blackbody radiation (see Section 4.2) to obtain the probability that his quantized oscillators would radiate energy when the blackbody was at temperature *T.* We do not derive the distribution, but illustrate its application and interpretation.

VIBRATIONAL ENERGY DISTRIBUTION

We apply the Boltzmann distribution to describe the probability of finding molecules in each of the vibrational states in a sample of CO held at temperature *T.* We describe the vibrational motions using the harmonic oscillator model, for which the allowed energy levels are

$$\varepsilon_n = \left(n + \frac{1}{2}\right)h\nu$$

where $n = 0, 1, 2, 3, \ldots$ and the vibrational frequency is related to the force constant by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

and μ is the reduced mass. These equations define the energy level diagram, which has uniformly spaced levels separated by

$$h\nu = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \qquad [9.21]$$

We calculate the reduced mass of $^{12}C^{16}O$ using the isotopic masses in Table 19.1 to be

$$\mu = \frac{m_C m_O}{m_C + m_O}$$

$$= \frac{(12.00)(15.99)\text{amu}}{27.99}\left(\frac{1\text{ g}}{6.02 \times 10^{23}\text{ amu}}\right)\left(\frac{1\text{ kg}}{10^3\text{ g}}\right)$$

$$\mu = 1.14 \times 10^{-26}\text{ kg}$$

The value of the force constant for CO is 1902 N m^{-1}, as measured in vibrational spectroscopy. The value of the energy level separation is then

$$h\nu = \left(\frac{6.63 \times 10^{-34}\text{ J s}}{2\pi}\right)\left(\frac{1.902 \times 10^3\text{ N m}^{-1}}{1.14 \times 10^{-26}\text{ kg}}\right)^{1/2}$$

$$h\nu = 4.52 \times 10^{-20}\text{ J}$$

The relative probability of finding molecules in the excited state n and in the ground state $n = 0$ is given by

$$\frac{P(n)}{P(0)} = \frac{C\exp(-\varepsilon_n/k_BT)}{C\exp(-\varepsilon_0/k_BT)} = \exp(-[\varepsilon_n - \varepsilon_0]/k_BT) \qquad [9.22]$$

Inserting the energy level expression for the harmonic oscillator gives

$$\frac{P(n)}{P(0)} = \exp(-[(n + \frac{1}{2})h\nu - \frac{1}{2}h\nu]/k_BT) = \exp(-nh\nu/k_BT) \qquad [9.23]$$

The relative populations of the first excited state $n = 1$ and the ground state are determined by the ratio $h\nu/k_BT$. We know from Chapter 4 that $h\nu$ is the quantum of vibrational energy needed to put a CO molecule in its first excited state, and we have calculated that value to be $h\nu = 4.52 \times 10^{-20}$ J. From Section 9.5 we know that the average kinetic energy of a molecule in the gas is $(3/2)k_BT$, which is $(1/2)k_BT$ for each of the x, y, and z directions of motion. Therefore, we interpret k_BT as a measure of the average energy available to each molecule in a gas at temperature *T.* So, the ratio $h\nu/k_BT$ determines whether there is sufficient energy in the gas to put the molecules into excited states. At 300 K, the value of k_BT is 4.14×10^{-21} J, which is a factor of 10 smaller than the vibrational quantum of CO. Inserting these numbers into Equation 9.23 gives the relative probability as 3.03×10^{-5}. This means that only 3 molecules in a group of 100,000 are in the first excited state at 300 K. At 1000 K, the value of k_BT is 1.38×10^{-20} J, which is closer to the value of the CO vibrational quantum and gives a relative population of 4.41×10^{-2}.

This case study shows that CO molecules do not have significant vibrational energy unless the temperature is quite high. This happens because CO has a triple bond and, therefore, a large force constant ($k = 1902$ N m^{-1}). The correlation between force constant and bond order in diatomic molecules is explained by molecular orbital theory, and is summarized in Figure 6.20. Other diatomic molecules will behave differently, as determined by their structure and the Boltzmann distribution.

EXAMPLE 9.8

Calculate the population of the first and second vibrational excited states, relative to the ground state, for Br_2 at $T = 300$ K and 1000 K. For Br_2, the measured vibrational frequency is $9.68 \times 10^{12}\ s^{-1}$. Interpret your results in relation to the chemical bond in Br_2.

SOLUTION

Use Equation 9.23 with $n = 1$ to obtain N_1/N_A and $n = 2$ to obtain N_2/N_A. It is convenient to evaluate the important quantities before substituting into the equation.

Evaluate the vibrational energy of Br_2:

$$h\nu = (6.63 \times 10^{-34}\ \text{J s})(9.68 \times 10^{12}\ \text{s}^{-1}) = 6.42 \times 10^{-21}\ \text{J}$$

Evaluate k_BT at 300 K and 1000 K:

$$k_BT = (300\ \text{K})(1.380 \times 10^{-23}\ \text{J K}^{-1}) = 4.14 \times 10^{-21}\ \text{J}$$

$$k_BT = (1000\ \text{K})(1.380 \times 10^{-23}\ \text{J K}^{-1}) = 1.38 \times 10^{-20}\ \text{J}$$

The population ratios at 300 K are:

$$\frac{P(1)}{P(0)} = \exp\left[-\frac{6.42 \times 10^{-21}\ \text{J}}{4.14 \times 10^{-21}\ \text{J}}\right] = 0.212$$

$$\frac{P(1)}{P(0)} = \exp\left[-\frac{2(6.42 \times 10^{-21}\ \text{J})}{4.14 \times 10^{-21}\ \text{J}}\right] = 0.045$$

The population ratios at 1000 K are:

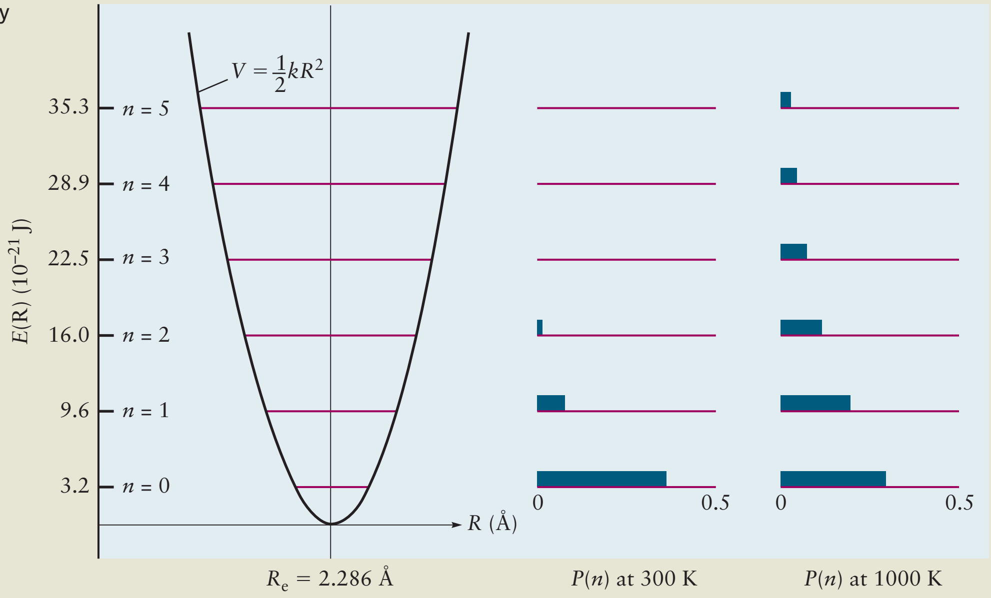
$$\frac{P(2)}{P(0)} = \exp\left[-\frac{6.42 \times 10^{-21}\ \text{J}}{1.38 \times 10^{-20}\ \text{J}}\right] = 0.628$$

$$\frac{P(2)}{P(0)} = \exp\left[-\frac{2(6.42 \times 10^{-21}\ \text{J})}{1.38 \times 10^{-20}\ \text{J}}\right] = 0.395$$

The distribution for the first six states at 300 K and 1000 K is shown in Figure 9.16.

The quantized energy vibration is much less for Br_2 than for CO for two reasons: the single bond in Br_2 has a much smaller force constant than the triple bond in CO, and the Br atoms are much more massive than C and O atoms.

FIGURE 9.16 The potential energy curve and energy levels for the harmonic oscillator model for CO.



(a) (b) (c)

Related Problems: 47, 48, 49, 50, 51, 52, 53, 54

9.7 Real Gases: Intermolecular Forces

The ideal gas law, $PV = nRT$, is a particularly simple example of an **equation of state**—an equation relating the pressure, temperature, number of moles, and volume to one another. Equations of state can be obtained from either theory or experiment. They are useful not only for ideal gases but also for real gases, liquids, and solids.

Real gases follow the ideal gas equation of state only at sufficiently low densities. Deviations appear in a variety of forms. Boyle's law, $PV = C$, is no longer satisfied at high pressures, and Charles's law, $V \propto T$, begins to break down at low temperatures. Deviations from the predictions of Avogadro's hypothesis appear for

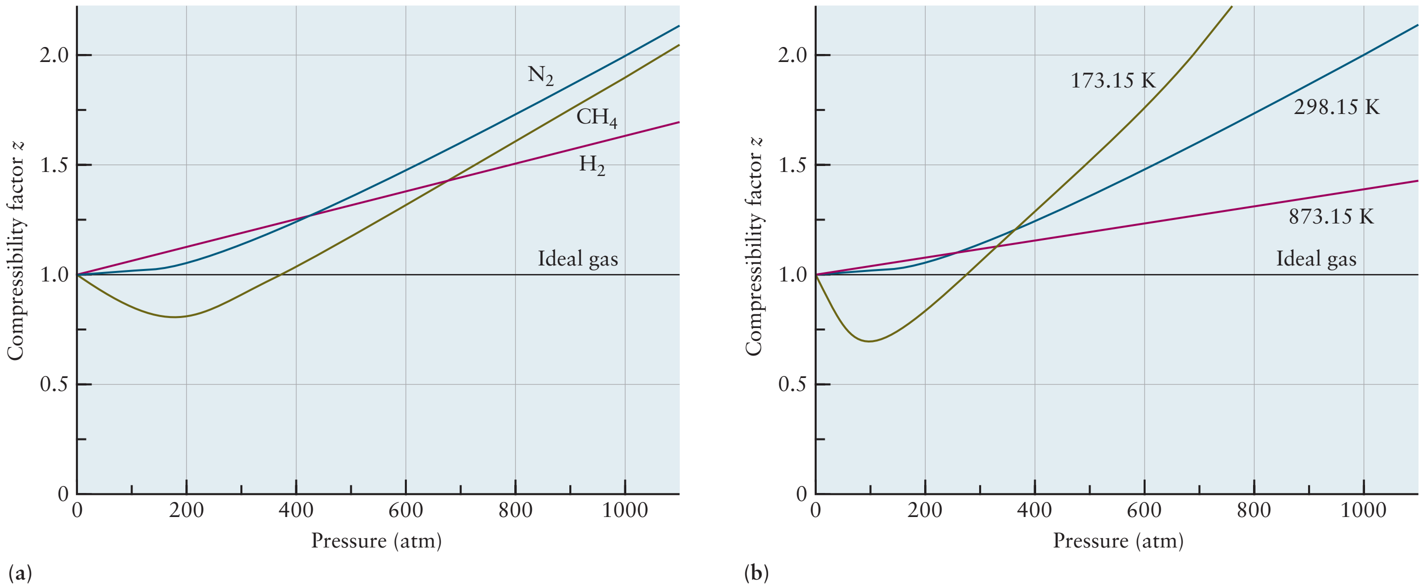


FIGURE 9.17 A plot of $z = PV/nRT$ against pressure shows deviations from the ideal gas law quite clearly, for an ideal gas, z is represented by the straight horizontal line. (a) Deviation of several real gases at 25°C. (b) Deviation of nitrogen at several temperatures.

real gases at moderate pressures. At atmospheric pressure, the ideal gas law is quite well satisfied for most gases, but for some with polar molecules (like water vapor and ammonia), there are deviations of 1 to 2%. The easiest way to detect these deviations is to calculate the **compressibility factor** z from experimental P-V-T data:

$$z = \frac{PV}{nRT} \qquad [9.24]$$

When z differs from 1 (Fig. 9.17), the ideal gas law is inadequate, and a more accurate equation of state is necessary.

The van der Waals Equation of State

One of the earliest and most important improvements on the ideal gas equation of state was proposed in 1873 by the Dutch physicist Johannes van der Waals. The **van der Waals equation of state** is:

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT \qquad [9.25a]$$

$$P = \frac{nRT}{V - nb} - a\frac{n^2}{V^2} \qquad [9.25b]$$

To obtain this equation, the ideal gas law—which ignores interactions between molecules—requires two modifications to describe the effects of the forces between molecules, which are repulsive at short distances and attractive at large distances. We know from Section 9.5 that pressure is determined by the product of the momentum transferred per collision with the walls of the container times the number of collisions per second. So, it is necessary to see how repulsive and attractive forces modify the collision rate away from the value it would have in the ideal gas. Because of repulsive forces, molecules cannot occupy the same space at the same time. They exclude other molecules from the volumes they occupy; in this way, the effective volume available to a given molecule is not V, but $V - nb$, where b is a

TABLE 9.3 van der Waals Constants of Several Gases

Name	Formula	*a* (atm L^2 mol^{-2})	*b* (L mol^{-1})
Ammonia	NH_3	4.170	0.03707
Argon	Ar	1.345	0.03219
Carbon dioxide	CO_2	3.592	0.04267
Hydrogen	H_2	0.2444	0.02661
Hydrogen chloride	HCl	3.667	0.04081
Methane	CH_4	2.253	0.04278
Nitrogen	N_2	1.390	0.03913
Nitrogen dioxide	NO_2	5.284	0.04424
Oxygen	O_2	1.360	0.03183
Sulfur dioxide	SO_2	6.714	0.05636
Water	H_2O	5.464	0.03049

constant describing the *excluded volume* per mole of molecules. This effect pushes the molecules away from each other and toward the walls, thereby increasing the rate of wall collisions. The result is a pressure higher than the ideal gas value, as shown in the first term of Equation 9.25b. Attractive forces hold pairs or groups of molecules together. Any tendency to cluster together reduces the effective number of independent molecules in the gas and, therefore, reduces the rate of collisions with the walls of the container. Having fewer wall collisions reduces the pressure below the ideal gas law prediction. Because this reduction depends on attractions between *pairs* of molecules, van der Waals argued that it should be proportional to the *square* of the number of molecules per unit volume (N^2/V^2) or, equivalently, proportional to n^2/V^2. Compared with the ideal gas, this intermolecular attraction reduces the pressure by an amount $a(n/V)^2$, where a is a positive constant that depends on the strength of the attractive forces. This effect gives the second term in Equation 9.25b. Rearranging Equation 9.25b gives the standard form of the van der Waals equation shown in Equation 9.25a.

The constants a and b are obtained by fitting experimental P-V-T data for real gases to Equation 9.25a or 9.25b (Table 9.3). The units for these constants are

$$a:\quad \text{atm L}^2\ \text{mol}^{-2}$$

$$b:\quad \text{L mol}^{-1}$$

when R has the units L atm mol^{-1} K^{-1}.

EXAMPLE 9.9

A sample of 8.00 kg gaseous nitrogen fills a 100-L flask at 300°C. What is the pressure of the gas, calculated from the van der Waals equation of state? What pressure would be predicted by the ideal gas equation?

SOLUTION

The molar mass of N_2 is 28 g mol^{-1}, so

$$n = \frac{8.00 \times 10^3\ \text{g}}{28.0\ \text{g mol}^{-1}} = 286\ \text{mol}$$

The temperature (in kelvins) is $T = 300 + 273 = 573$ K, and the volume, V, is 100 L. Using $R = 0.08206$ L atm mol^{-1} K^{-1} and the van der Waals constants for nitrogen given in Table 9.3, we calculate $P = 151 - 11 = 140$ atm. If the ideal gas law is used instead, a pressure of 134 atm is calculated. This illustrates the magnitude of deviations from the ideal gas law at higher pressures.

Related Problems: 55, 56, 57, 58

The effects of the two van der Waals parameters are clearly apparent in the compressibility factor for this equation of state:

$$z = \frac{PV}{nRT} = \frac{V}{V - nb} - \frac{a}{RT}\frac{n}{V} = \frac{1}{1 - bn/V} - \frac{a}{RT}\frac{n}{V} \qquad [9.26]$$

Repulsive forces (through b) increase z above 1, whereas attractive forces (through a) reduce z.

We illustrate the effects of a by comparing Equation 9.26 with the experimental data for the compressibility factor shown in Figure 9.17a. At lower pressures, for example 200 atm, the intermolecular forces reduce z for CH_4 to a value significantly below the ideal gas value. For N_2, the effect that decreases z is readily apparent but it is smaller than the effect that increases z. For H_2, the effect that decreases z is completely dominated by the forces that increase z. These results are consistent with the a-parameter value for CH_4 being about twice that for N_2 and about 10 times that for H_2 (see Table 9.3). The values of a originate in the structure of the molecules and vary significantly between highly polar molecules such as H_2O and nonpolar molecules such as H_2.

The constant b is the volume excluded by 1 mol of molecules and should therefore be close to V_m, the volume per mole in the liquid state, where molecules are essentially in contact with each other. For example, the density of liquid nitrogen is 0.808 g cm^{-3}. One mole of N_2 weighs 28.0 g, so

$$V_m \text{ of } N_2(\ell) = \frac{28.0 \text{ g mol}^{-1}}{0.808 \text{ g cm}^{-3}} = 34.7 \text{ cm}^3 \text{ mol}^{-1}$$
$$= 0.0347 \text{ L mol}^{-1}$$

This is reasonably close to the van der Waals b parameter of 0.03913 L mol^{-1}, obtained by fitting the equation of state to P-V-T data for nitrogen. In Table 9.3, the values for b are all quite similar. All the molecules in Table 9.3 are about the same size and have similar values of molar volume in the liquid state.

Intermolecular Forces

Deeper understanding of the attractive force parameter, a, and the excluded volume per mole, b, comes from examination of the forces acting between the atoms or molecules in a gas. As a pair of molecules approach one another, the forces between them generate potential energy, which competes with the kinetic energy associated with their speeds. This potential energy can increase the molar volume through intermolecular repulsions, or decrease the pressure by temporarily attracting molecules to form dimers and so reducing the rate of collisions with the walls. The potential energy is our means to describe systematically how intermolecular forces cause these two effects. The noble gases provide the simplest example. As two noble gas atoms approach one another, attractive forces dominate until the distance between their centers, R, becomes short enough for the repulsive forces to begin to become significant. If the atoms are forced still closer together, they repel each other with a strongly increasing force as the distance between them is reduced. These interactions can be described by a **potential energy curve** $V(R)$ (see Section 3.5, Section 6.2.5, and Appendix B) such as that shown for argon in Figure 9.18. If two molecules can lower their energy by moving closer together, then a net attractive force exists between them; if they can lower their energy only by moving apart, there is a net repulsive force. Graphically, this means that the force acting between the molecules is given by the negative slope (or derivative) of the potential energy curve $V(R)$. The force changes from attractive to repulsive at the minimum of $V(R)$, where the net force between atoms is zero. Potential energy curves for atoms are generated by fitting equations for $V(R)$ to measured properties of real gases. More accurate versions come from experiments in which beams of atoms collide with one another.

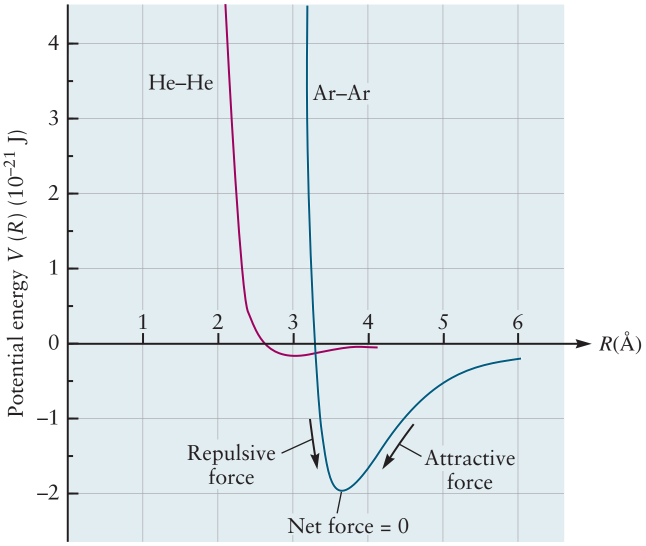


FIGURE 9.18 Potential energy curves $V(R)$ for pairs of helium atoms (red) and pairs of argon atoms (blue) obtained from atomic beam collision studies. At any point, the force between atoms is the negative of the slope of V (see Section 3.5, Section 6.2.5, and Appendix B.2). In regions where the slopes of the curves are negative, the atoms repel each other. In regions where the slopes are positive, the atoms attract one another. The greater well depth for Ar arises from stronger intermolecular attractions, and the location of the minimum for Ar at larger R correlates roughly with relative molecular size.

For many purposes, the detailed shape of the potential is less important than two characteristic parameters: the depth and location of the potential minimum. A simple expression frequently used to model these interactions between atoms is the **Lennard–Jones potential:**

$$V_{\mathrm{LJ}}(R) = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right] \qquad [9.27]$$

where ε is the depth and σ is the distance at which $V(R)$ passes through zero. This potential has an attractive part, proportional to R^{-6}, and a repulsive part, proportional to R^{-12}. The minimum is located at $2^{1/6}\sigma$, or 1.22σ. Table 9.4 lists Lennard–Jones parameters for a number of atoms. Note that the depth and range of the potential increase for the heavier noble-gas atoms. Molecules such as N_2 that are nearly spherical can also be described approximately with Lennard–Jones potentials. The two parameters ε and σ in the Lennard–Jones potential, like the van der Waals parameters a and b, are simple ways of characterizing the interactions between molecules in real gases.

The Lennard–Jones potential and the Boltzmann distribution (see Section 9.6) together explain how deviations from ideal gas behavior depend on temperature. Qualitatively, the most important effect is the ratio of the well depth ε to k_BT. When T is low enough to make $k_BT \ll \varepsilon$, a pair of molecules remain close together sufficiently long to reduce the rate of wall collisions, and thereby reduce the pressure below its ideal gas value. When T is such that $k_BT \gg \varepsilon$, the molecules experience only the repulsive part of the L–J potential, and the pressure is increased

TABLE 9.4 Lennard–Jones Parameters for Atoms and Molecules

Substance	σ(m)	ε(J)
He	2.56×10^{-10}	1.41×10^{-22}
Ne	2.75×10^{-10}	4.92×10^{-22}
Ar	3.40×10^{-10}	1.654×10^{-21}
Kr	3.60×10^{-10}	2.36×10^{-21}
Xe	4.10×10^{-10}	3.06×10^{-21}
H_2	2.93×10^{-10}	5.11×10^{-22}
O_2	3.58×10^{-10}	1.622×10^{-21}
CO	3.76×10^{-10}	1.383×10^{-21}
N_2	3.70×10^{-10}	1.312×10^{-21}
CH_4	3.82×10^{-10}	2.045×10^{-21}

above its ideal gas value. These effects are illustrated in Figure 9.17b, which shows that at low pressure the compressibility factor for N_2 is dominated by attractive forces at 173.15 K and by repulsive forces at 873.15 K.

The Lennard–Jones potential gives insight into the roles of the average kinetic energy of molecules (indicated by k_BT) and the potential energy between molecules (indicated by ε) in gases. At 300 K, the value of k_BT is 4.14×10^{-21} J, which is comparable to and slightly larger than the well depths for typical gases listed in Table 9.4. Consequently, the average kinetic energy of a molecule is larger than the greatest value of the potential energy that can occur between a pair of molecules. Because the molecules are only rarely close together in gases at ordinary pressures, the potential energy per pair averaged over all pairs in the gas is much smaller than the average kinetic energy. So, the behavior of gases is determined primarily by the average kinetic energy of the molecules.

A DEEPER LOOK

9.8 Molecular Collisions and Rate Processes

The kinetic theory we have developed can be applied to several important properties of gases. A study of the rates at which atoms and molecules collide with a wall and with one another helps to explain phenomena ranging from isotope separation based on gaseous diffusion to gas-phase chemical kinetics.

Molecule-Wall Collisions

Let's call Z_w the rate of collisions of gas molecules with a section of wall of area A. A full mathematical calculation of Z_w requires integral calculus and solid geometry. We present instead some simple physical arguments to show how this rate depends on the properties of the gas.

First of all, Z_w should be proportional to the area A, because doubling the area will double the number of collisions with the wall. Second, Z_w should be proportional to the average molecular speed, $\bar{u}$, because molecules moving twice as fast will collide twice as often with a given wall area. Finally, the wall collision rate should be proportional to the number density, N/V, because twice as many molecules in a given volume will have twice as many collisions with the wall. All of these arguments are consistent with the kinetic theory of gases and are confirmed by the full mathematical analysis. We conclude that

$$Z_w \propto \frac{N}{V}\bar{u}A$$

Note that the units of both sides is s^{-1}, as required for these expressions to represent a rate. The proportionality constant can be calculated from a complete analysis of the directions from which molecules impinge on the wall; it turns out to have the value $\frac{1}{4}$. So the wall collision rate is

$$Z_w \propto \frac{1}{4}\frac{N}{V}\bar{u}A = \frac{1}{4}\frac{N}{V}\sqrt{\frac{8RT}{\pi \mathcal{M}}}A \qquad [9.28]$$

We have used the result for $\bar{u}$ given earlier in Equation 9.19. This simple equation has many applications. It sets an upper limit on the rate at which a gas may react with a solid. It is also the basis for calculating the rate at which molecules effuse through a small hole in the wall of a vessel.

EXAMPLE 9.10

Calculate the number of collisions that oxygen molecules make per second on 1.00 cm^2 of the surface of the vessel containing them if the pressure is 1.00×10^{-6} atm and the temperature is 25°C (298 K).

SOLUTION

First compute the quantities that appear in the equation for Z_w:

$$\frac{N}{V} = \frac{N_A n}{V} = \frac{N_A P}{RT}$$

$$= \frac{(6.022 \times 10^{23}\ \text{mol}^{-1})(1.00 \times 10^{-6}\ \text{atm})}{(0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}$$

$$= 2.46 \times 10^{16}\ \text{L}^{-1} = 2.46 \times 10^{19}\ \text{m}^{-3}$$

$$A = 1.00\ \text{cm}^2 = 1.00 \times 10^{-4}\ \text{m}^2$$

$$\bar{u} = \sqrt{\frac{8RT}{\pi \mathcal{M}}}$$

$$= \sqrt{\frac{8(8.3145\ \text{J mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}{\pi(32.00 \times 10^{-3}\ \text{kg mol}^{-1})}}$$

$$= 444\ \text{m s}^{-1}$$

The collision rate is then

$$Z_w = \frac{1}{4}\frac{N}{V}\bar{u}A$$

$$= \tfrac{1}{4}(2.46 \times 10^{19}\ \text{m}^{-3})(444\ \text{m s}^{-1})(1.00 \times 10^{-4}\ \text{m}^2)$$

$$= 2.73 \times 10^{17}\ \text{s}^{-1}$$

Related Problems: 59, 60

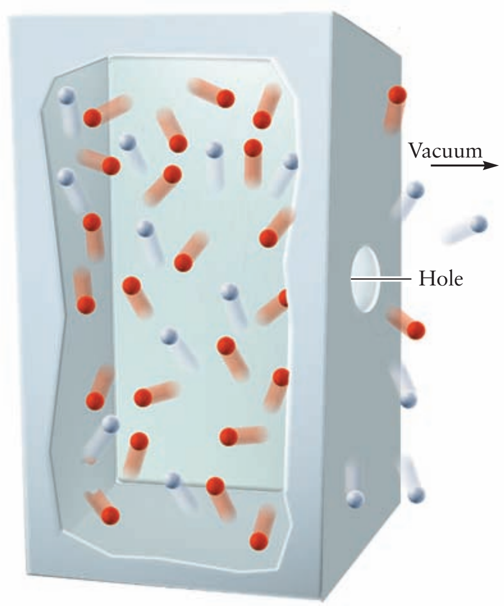


FIGURE 9.19 A small hole in the box permits molecules to effuse out into a vacuum. The less massive particles (here, helium atoms, red) effuse at greater rates than the more massive oxygen molecules (purple) because their speeds are greater on the average.

Equation 9.28 is the basis of explaining **Graham's law of effusion.** In 1846, Thomas Graham showed experimentally that the rate of effusion of a gas through a small hole into a vacuum (Fig. 9.19) is inversely proportional to the square root of its molar mass. Assuming that different gases are studied at the same temperature and pressure, their number density, N/V, is the same and the rate of effusion of each gas depends only on the factor $1/\sqrt{\mathcal{M}}$ in Equation 9.28, exactly as observed by Graham. Explaining this experimental result is yet another success for the kinetic theory of gases.

Graham's law also describes the effusion of a mixture of two gases through a small hole. The ratio of the rates of effusion of the two species, A and B, is

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{\dfrac{1}{4}\dfrac{N_A}{V}\sqrt{\dfrac{8RT}{\pi\mathcal{M}_A}}\,A}{\dfrac{1}{4}\dfrac{N_B}{V}\sqrt{\dfrac{8RT}{\pi\mathcal{M}_B}}\,A} \qquad [9.29]$$

$$= \frac{N_A}{N_B}\sqrt{\frac{\mathcal{M}_B}{\mathcal{M}_A}}$$

This ratio is equal to the ratio of the numbers of molecules of the two species effusing through the hole in a short time interval. N_A and N_B are the number of molecules of species A and B, respectively. The emerging gas is enriched in the lighter component because lighter molecules effuse more rapidly than heavier ones. If B is heavier than A, the **enrichment factor** is $\sqrt{\mathcal{M}_B/\mathcal{M}_A}$ for the lighter species, A.

EXAMPLE 9.11

Calculate the enrichment factors from effusion for a mixture of $^{235}UF_6$ and $^{238}UF_6$, uranium hexafluoride with two different uranium isotopes. The atomic mass of ^{235}U is 235.04, and that of ^{238}U is 238.05. The atomic mass of fluorine is 19.00.

SOLUTION

The two molar masses are

$$\mathcal{M}(^{238}UF_6) = 238.05 + 6(19.00) = 352.05\ \text{g mol}^{-1}$$

$$\mathcal{M}(^{235}UF_6) = 235.04 + 6(19.00) = 349.04\ \text{g mol}^{-1}$$

$$\text{enrichment factor} = \sqrt{\frac{\mathcal{M}(^{238}UF_6)}{\mathcal{M}(^{235}UF_6)}} = \sqrt{\frac{352.05\ \text{g mol}^{-1}}{349.04\ \text{g mol}^{-1}}}$$

$$= 1.0043$$

Related Problems: 61, 62

Graham's law of effusion holds true only if the opening in the vessel is small enough and the pressure low enough that most molecules follow straight-line trajectories through the opening without colliding with one another. A related but more complex phenomenon is **gaseous diffusion through a porous barrier.** This differs from effusion in that molecules undergo many collisions with one another and with the barrier during their passage through it. Just as in effusion, the diffusion rate is inversely proportional to the square root of the molar mass of the gas. But the reasons for this dependence are not those outlined for the effusion process. If a mixture of gases is placed in contact with a porous barrier, the gas passing through is enriched in the lighter component, A, by a factor of $\sqrt{\mathcal{M}_B/\mathcal{M}_A}$, and the gas remaining behind is enriched in the heavier component.

In order to develop the atomic bomb, it was necessary to separate the more easily fissionable isotope ^{235}U from ^{238}U. Because the natural abundance of ^{235}U is only 0.7%, its isolation

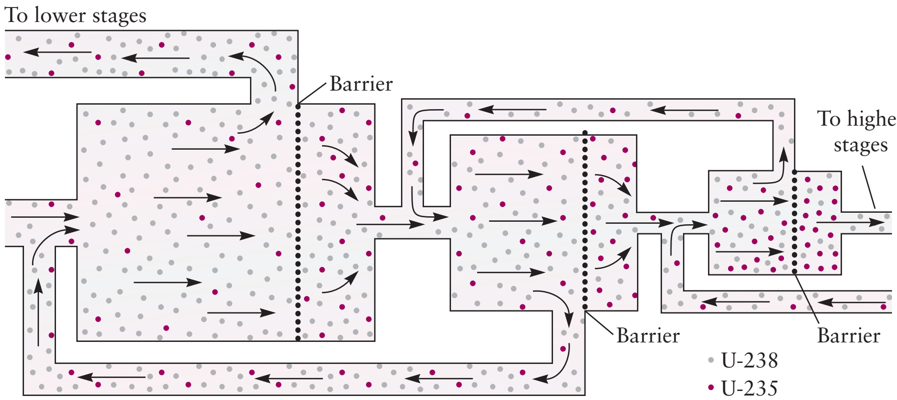


FIGURE 9.20 Schematic of one of 3122 diffusion stages in the gaseous diffusion plant at Oak Ridge National Laboratory. Gaseous UF_6 entering the left side of the stage is progressively enriched as it moves through the stage from left to right as indicated by an increase in the number of red dots representing $^{235}UF_6$ molecules. There are three diffusion barriers in each stage and gases are recycled through the barriers within a stage, as well as between stages, multiple times as shown by the arrows flowing back to the left.

in nearly pure form was a daunting task. The procedure adopted was to react uranium with F_2 gas to form the relatively volatile compound UF_6 (boiling point, 56°C), which can be enriched in ^{235}U by passing it through a porous barrier. As shown in Example 9.12, each passage gives an enrichment factor of only 1.0043. So, successive passage through many such barriers is necessary to provide sufficient enrichment of the ^{235}U component. A multi-state gaseous diffusion chamber was constructed in a short time at the Oak Ridge National Laboratories, and the enriched ^{235}U was used in the first atomic bomb. Similar methods are still used today to enrich uranium for use as fuel in nuclear power plants (Fig. 9.20).

EXAMPLE 9.12

How many diffusion stages are required if ^{235}U is to be enriched from 0.70 to 7.0% by means of the gaseous UF_6 diffusion process?

SOLUTION

From Example 9.11, the enrichment factor per stage is 1.0043; thus, the first stage is described by the relation

$$\left(\frac{N^{235}UF_6}{N^{238}UF_6}\right)_1 = \left(\frac{N^{235}UF_6}{N^{238}UF_6}\right)_0 (1.0043)$$

where the subscripts 0 and 1 denote the initial concentration and that after the first stage, respectively. The ratio of the numbers after n stages satisfies the equation

$$\left(\frac{N^{235}UF_6}{N^{238}UF_6}\right)_n = \left(\frac{N^{235}UF_6}{N^{238}UF_6}\right)_0 (1.0043)^n$$

$$\frac{7.0}{93.0} = \frac{0.70}{99.30}(1.0043)^n$$

$$10.677 = (1.0043)^n$$

This equation can be solved by taking logarithms of both sides (see Appendix C):

$$\log_{10}(10.677) = n \log_{10}(1.0043)$$

$$1.02845 = 0.0018635n$$

$$n = 552 \text{ stages}$$

Related Problems: 63, 64

Molecule–Molecule Collisions

Collisions lie at the very heart of chemistry, because chemical reactions can occur only when molecules collide with one another. The kinetic theory of gases provides methods for estimating the frequency of molecular collisions and the average distance traveled by a molecule between collisions, both important in understanding the rates of chemical reactions (See Chapter 18).

We assume molecules are approximately spherical, with diameters, d, on the order of 10^{-10} m (see Section 2.1). We initially suppose that a particular molecule moves through a gas of stationary molecules of the same diameter. Such a molecule "sweeps out" a cylinder with cross-sectional area, $A = \pi d^2$ (Fig. 9.21). This particular molecule collides with any molecule whose center lies inside the cylinder, within a distance, d, of the center of the moving molecule. In 1 second, the length of such a cylinder is $\bar{u}\,\Delta t = \bar{u} \times 1$ s, where $\bar{u}$ is the average molecular speed. It does not matter that the moving molecule is scattered in another direction when it collides with other molecules; these little cylinders are merely joined together, end to end, to define a cylinder whose length is $\bar{u} \times 1$ s.

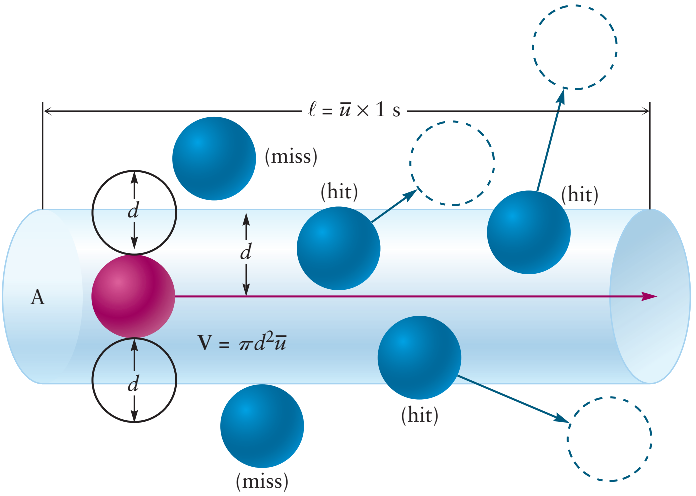


FIGURE 9.21 An average molecule (red) sweeps out a cylinder of volume $\pi d^2 \bar{u}$ in 1 second. It will collide with any molecules whose centers lie within the cylinder. Using this construction, we can calculate the rate of collisions with other molecules.

In 1 second, the moving molecule therefore sweeps out the volume

$$V_{cyl} = \pi d^2 \bar{u}$$

If N/V is the number of molecules per unit volume in the gas (the number density of the gas), then the number of collisions per second experienced by the moving molecule is

$$\text{collision rate} = Z_1 = \frac{N}{V} V_{cyl} = \frac{N}{V} \pi d^2 \bar{u} \quad \text{(approximately)}$$

Actually, this equation is only approximate, because the other molecules are not standing still but are moving. A full calculation gives an extra factor of $\sqrt{2}$:

$$Z_1 = \sqrt{2} \frac{N}{V} \pi d^2 \bar{u}$$

Inserting the result for $\bar{u}$ from Equation 9.19 gives

$$\boxed{Z_1 = 4 \frac{N}{V} d^2 \sqrt{\frac{\pi RT}{\mathcal{M}}}} \qquad [9.30]$$

EXAMPLE 9.13

Calculate the collision frequency for (**a**) a molecule in a sample of oxygen at 1.00 atm pressure and 25°C, and (**b**) a molecule of hydrogen in a region of interstellar space where the number density is 1.0×10^{10} molecules per cubic meter and the temperature is 30 K. Take the diameter of O_2 to be 2.92×10^{-10} m and that of H_2 to be 2.34×10^{-10} m.

SOLUTION

$$\frac{N}{V} = \frac{N_A P}{RT} = \frac{(6.022 \times 10^{23}\ \text{mol}^{-1})(1.00\ \text{atm})}{(0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1})(298\ \text{K})}$$

$$= 2.46 \times 10^{+22}\ \text{L}^{-1} = 2.46 \times 10^{25}\ \text{m}^{-3}$$

In Example 9.10, we found $\bar{u}$ to be 444 m s^{-1}. Thus, the collision frequency is

$$Z_1 = \sqrt{2}\pi(2.46 \times 10^{25}\ \text{m}^{-3}) \times (2.92 \times 10^{-10}\ \text{m})^2(444\ \text{m}^{-1})$$

$$= 4.14 \times 10^9\ \text{s}^{-1}$$

This is the average number of collisions experienced by each molecule per second.

(**b**) An analogous calculation gives

$$Z_1 = 1.4 \times 10^{-6}\ \text{s}^{-1}$$

In other words, the average molecule under these conditions waits 7.3×10^5 seconds, or 8.5 days, between collisions.

Mean Free Path and Diffusion

Z_1 is the rate at which a particular molecule collides with other molecules. Its inverse, Z_1^{-1}, therefore measures the average time between collisions. During this interval, a molecule travels an average distance $\bar{u}\, Z_1^{-1}$ which is called the **mean free path,** λ.

$$\lambda = \bar{u}Z_1^{-1} = \frac{\bar{u}}{\sqrt{2}(N/V)\pi d^2\bar{u}} = \frac{1}{\sqrt{2}\pi d^2 N/V} \qquad [9.31]$$

The mean free path, unlike the collision frequency, does not depend on the molar mass. The mean free path must be much larger than the molecular diameter for a gas to show ideal gas behavior. For a molecule of diameter 3×10^{-10} m, the mean free path at 25°C and atmospheric pressure is 1×10^{-7} m, which is 300 times larger.

Molecules in a gas move in straight lines only for rather short distances before they are deflected by collisions and change direction (Fig. 9.22). Because each molecule follows a zigzag course, they take more time to travel a particular net distance from their starting points than they would if there were no collisions. This fact helps explain why diffusion is slow in gases. Recall that at room temperature the speed of a molecule is on the order of 1×10^3 m s^{-1}. If molecules traveled in straight-line trajectories, a perfume released in one part of a room would be noticed across the room almost instantaneously. Instead, there is a time lapse because the molecules follow irregular paths that we call "random walks."

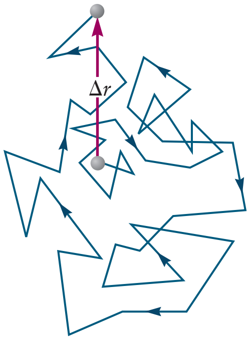


FIGURE 9.22 A gas molecule follows a straight-line path for only a short time before undergoing a collision, so its overall path is a zigzag one. The displacement Δ*r* of a particular molecule in time, Δ*t*, is shown. The path taken by the molecules is traced out in blue, and the red arrow represents the total displacement during the period Δ*t*. The mean-square displacement $\overline{\Delta r^2}$, is equal to 6*Dt*, where *D* is the diffusion constant of the molecules in the gas.

We can describe diffusion in a gas using averaged quantities such as the mean-square displacement, $\overline{\Delta r^2} = \overline{\Delta x^2} + \overline{\Delta y^2} + \overline{\Delta z^2}$, which is analogous to the mean-square speed considered earlier. If there are no gas currents to perturb the motion of the gas molecules—a rather strenuous condition requiring strict isolation of the experiment from the surroundings—then $\overline{\Delta r^2}$ is found to be proportional to the time elapsed, t:

$$\overline{\Delta r^2} = 6Dt \qquad [9.32]$$

The proportionality constant is $6D$, where D is the **diffusion constant** of the molecules. So, the root-mean-square displacemen $\sqrt{\overline{\Delta r^2}}$ is equal to $\sqrt{6Dt}$.

The diffusion constant has units of $\text{m}^2\ \text{s}^{-1}$. It is proportional to the mean free path, λ, and to the mean molecular speed $\bar{u}$, but the proportionality constant is difficult to calculate in general. For the simplest case, a single-component gas, the proportionality constant is $3\pi/16$, so

$$D = \frac{3\pi}{16}\lambda\bar{u} = \frac{3\pi}{16}\sqrt{\frac{8RT}{\pi\mathcal{M}}}\,\frac{1}{\sqrt{2}\pi d^2 N/V}$$

$$= \frac{3}{8}\sqrt{\frac{RT}{\pi\mathcal{M}}}\,\frac{1}{d^2 N/V} \qquad [9.33]$$

EXAMPLE 9.14

Calculate the mean free path and the diffusion constant for the molecules in Example 9.13.

SOLUTION

(**a**) The mean free path is

$$\lambda = \frac{1}{\sqrt{2}\pi(2.92 \times 10^{-10}\ \text{m})^2(2.46 \times 10^{25}\ \text{m}^{-1})}$$

$$= 1.07 \times 10^{-7}\ \text{m}$$

The diffusion constant is

$$D = \frac{3\pi}{16}\lambda\bar{u} = \frac{3\pi}{16}(1.07 \times 10^{-7}\ \text{m})(444\ \text{m s}^{-1})$$

$$= 2.80 \times 10^{-5}\ \text{m}^2\ \text{s}^{-1}$$

(**b**) An analogous calculation for an average molecule of H_2 in interstellar space gives

$$\lambda = 4.1 \times 10^8\ \text{m}$$

For comparison, the distance from the Earth to the moon is 3.8×10^8 m. The diffusion constant is

$$D = 1.4 \times 10^{11}\ \text{m}^2\ \text{s}^{-1}$$

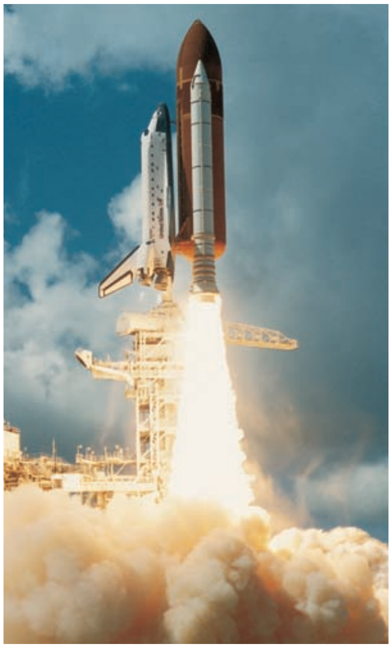
Related Problems: 65, 66

CHAPTER SUMMARY

Gases provide the simplest opportunity for relating macroscopic properties of matter to the structure, motions, and interactions of molecules. Because molecules in gases are quite far apart most of the time, we can neglect intermolecular forces and represent the molecules as point masses that have only kinetic energy and collide with the walls of the container but not with each other. The simplest treatment of this physical model predicts the ideal gas law, which was discovered empirically. More elaborate mathematical treatments of the same model produce the full probability distribution for molecular speeds. From this distribution, various average quantities can be calculated and used to interpret numerous experimental phenomena in gases at low density. At higher density, intermolecular forces can no longer be neglected. Their effect is described systematically by the intermolecular potential energy function, which includes both the attractive and repulsive effects. The well depth and location of the minimum in the potential energy curve are very useful parameters for summarizing these effects. They provide deeper insight into the attractive and repulsive constants that are obtained by fitting the van der Waals equation of state to empirical data. It is especially interesting to see that the value of k_BT at room temperature is larger than the well depths of the intermolecular potential. Because the molecules are far apart most of the time, the average kinetic energy per molecule exceeds the average potential energy per molecule. So, the properties of gases at room temperature are determined by the kinetic energy of the molecular motions.

CUMULATIVE EXERCISE

Ammonium Perchlorate


NASA

A space shuttle taking off.

Ammonium perchlorate (NH_4ClO_4) is a solid rocket fuel used in space shuttles. When heated above 200°C, it decomposes to a variety of gaseous products, of which the most important are N_2, Cl_2, O_2, and water vapor.

(a) Write a balanced chemical equation for the decomposition of NH_4ClO_4, assuming the products just listed are the only ones generated.

(b) The sudden appearance of hot gaseous products in a small initial volume leads to rapid increases in pressure and temperature, which give the rocket its thrust. What total pressure of gas would be produced at 800°C by igniting 7.00×10^5 kg NH_4ClO_4 (a typical charge of the booster rockets in the space shuttle) and allowing it to expand to fill a volume of 6400 m^3 (6.40×10^6 L)? Use the ideal gas law.

(c) Calculate the mole fraction of chlorine and its partial pressure in the mixture of gases produced.

(d) The van der Waals equation applies strictly to pure real gases, not to mixtures. For a mixture like the one resulting from the reaction of part (a), it may still be possible to define effective a and b parameters to relate total pressure, volume, temperature, and total number of moles. Suppose the gas mixture has $a = 4.00$ atm L^2 mol^{-2} and $b = 0.0330$ L mol^{-1}. Recalculate the pressure of the gas mixture in part (b) using the van der Waals equation. Why is the result smaller than that in part (b)?

(e) Calculate and compare the root-mean-square speeds of water and chlorine molecules under the conditions of part (b).

(f) The gas mixture from part (b) cools and expands until it reaches a temperature of 200°C and a pressure of 3.20 atm. Calculate the volume occupied by the gas mixture after this expansion has occurred. Assume ideal gas behavior.

Answers

(a) $2\ NH_4ClO_4(s) \longrightarrow N_2(g) + Cl_2(g) + 2\ O_2(g) + 4\ H_2O(g)$

(b) 328 atm

(c) $X_{Cl_2} = \frac{1}{8} = 0.125$ (exactly); $P_{Cl_2} = 41.0$ atm

(d) 318 atm. The real pressure is less than that calculated using the ideal gas law because half of the products are water molecules that have very strong intermolecular attractions, leading to the large value of the *a* parameters for the gas mixture.

(e) $u_{rms}(H_2O) = 1220\ m\ s^{-1}$; $u_{rms}(Cl_2) = 614\ m\ s^{-1}$

(f) $2.89 \times 10^5\ m^3$

CHAPTER REVIEW

- Composition of the Air

Roughly 78% N_2, 21% O_2, 1% Ar.
CO_2 is 380 ppm and increasing.

- Pressure and Temperature of Gases and the Ideal Gas Law

Pressure is defined as force/area measured in atm, bar, pascal, and torr.
The empirical gas laws of Boyle, Charles, and Avogadro combine to give the ideal gas law: $PV = nRT$.

- Gaseous Mixtures are described by Dalton's Law

$P_A = n_ART/V$
$X_A = n_A/n_{tot}$
$P_A = X_AP_{tot}$

- The Kinetic Theory of Gases

Molecules are assumed to be widely separated point masses that interact only during collisions, move randomly with a distribution of speeds, and experience elastic collisions with walls
The square of the speed is the sum of the squares of velocity components $u^2 = v_x^2 + v_y^2 + v_z^2$
The rate of momentum transfer = (rate of collisions along any axis) × (momentum transfer per collision)
The total number of wall collisions relates the pressure to the average kinetic energy per molecule: $PV = (1/3)Nm\overline{u^2}$
The kinetic theory of gases predicts the ideal gas law from a simple molecular model
Connecting the results of the kinetic theory of gases to the ideal gas law gives a microscopic, mechanical interpretation of temperature, the average kinetic energy per mole is equal to 3/2 RT.

- The Maxwell–Boltzmann (MB) distribution

The MB distribution gives the probability of finding molecules with each value of speed from zero to infinity, as a function of the temperature of the gas. The MB distribution has the mathematical form $f(u) \propto u^2 \exp(-mu^2/2k_BT)$.

At a given temperature, lighter molecules have higher speeds than heavier molecules. The ratio of speeds is related to the ratio of masses as $u_2/u_1 = \sqrt{M_1/M_2}$.

The MB distribution gives low probability for very low and very high speeds, with a maximum called the most probable speed u_{mp}, which occurs at an intermediate value.

As temperature increases, the maximum shifts to higher speed values, and the distribution broadens.

The MB distribution is not symmetrical about its maximum value because it is the product of two competing factors: the statistical weight for each value of speed, and the number of ways of achieving that speed. The total probability is slightly greater for speed values higher than u_{mp} than for speed values lower than u_{mp}.

Like any nonsymmetrical probability distribution, the MB speed distribution can be characterized by several different single numbers: average speed $\bar{u}$, most probable speed u_{mp}, and root-mean-square speed u_{rms}. Because the MB has greater total probability to the high side of the most probable speed, these three numbers have this order: $u_{\text{mp}} < \bar{u} < u_{\text{rms}}$. We most often use $\bar{u}$, the last in applications of the kinetic theory.

- Rates of molecule-wall and molecule-molecule collisions from the kinetic theory of gases depend on the average molecular speed $\bar{u}$.

  The rate of molecular collisions with a wall of area A given by $Z_w = \frac{1}{4}\frac{N}{V}\bar{u}A$ determines the rate of gaseous effusion through a small aperture and sets an upper bound for the rate of gas-surface chemical reactions

  The rate of molecule-molecule collisions given by $Z_1 = \sqrt{2}\,(N/V)\pi d^2\bar{u}$ estimates the upper bound of gas phase chemical reaction rates and calculates the distance a molecule travels between collisions as well as the diffusion coefficient in gases

- The Boltzmann distribution

  The probability is weighted by the energy of the state and the temperature of the gas $P(n) = C\exp(-\varepsilon_n/k_BT)$

  The relative populations of two quantum states is given by $\frac{P(n)}{P(0)} = \frac{C\exp(-\varepsilon_n/k_BT)}{C\exp(-\varepsilon_0/k_BT)} = \exp(-[\varepsilon_n - \varepsilon_0]/k_BT)$

- Deviations from ideal gas behavior and the van der Waals equation of state

  Real gases do not obey the ideal gas law because attractive and repulsive forces between molecules introduce potential energy that competes with the purely kinetic energy of translation from which the ideal gas law arises.

  The van der Waals equation of state is the simplest two-parameter equation of state for real gases. A simple physical model underlies the form of the equation and its two parameters.

  Molecules have finite size and exclude volume to other molecules: the a parameter.

  Molecules attract one another and reduce wall collision rate: the b parameter.

  The equation is $P = \frac{nRT}{V - nb} - a\frac{n^2}{V^2}$

  The Lennard–Jones potential energy function systematically describes the attractive and repulsive forces at all distances in terms of ε the well depth and σ the location of the potential minimum.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Write chemical equations for several reactions that lead to gas formation (Section 9.1, Problems 1–4).
2. Describe how pressure and temperature are defined and measured (Section 9.2, Problems 5–10).
3. Use the ideal gas law to relate pressure, volume, temperature, and number of moles of an ideal gas and to do stoichiometric calculations involving gases (Section 9.3, Problems 19–32).
4. Use Dalton's law to calculate partial pressures in gas mixtures (Section 9.4, Problems 33–38).
5. Use the Maxwell–Boltzmann distribution of molecular speeds to calculate root-mean-square, most probable, and average speeds of molecules in a gas (Section 9.5, Problems 41–44).
6. Describe the connection between temperature and the speeds or kinetic energies of the molecules in a gas (Section 4.5, problems 45–46).
7. Use the Boltzmann distribution to determine the relative population of two quantum states in a gas at temperature T (Section 9.6, Problems 47–54).
8. Use the van der Waals equation to relate the pressure, volume, temperature, and number of moles of a nonideal gas (Section 9.7, Problems 55–58).
9. Discuss how forces between atoms and molecules vary with distance (Section 9.7).
10. Calculate the rate of collisions of molecules with a wall, and from that calculation determine the effusion rate of a gas through a small hole of known area (Section 9.8, Problems 59–60).
11. Calculate the enrichment factor for lighter molecules when a gas consisting of a mixture of light and heavy molecules effuses through a small aperture in a vessel wall (Section 9.8, Problems 61–64).
12. Calculate the collision frequency, mean free path, and diffusion constant for gases (Section 9.8, Problems 65–66).

KEY EQUATIONS

$P = \rho g h$ **(Section 9.2)**

$PV = C$ (fixed temperature and fixed amount of gas) **(Section 9.2)**

$PV = 22.414 \text{ L atm}$ (for 1 mol gas at 0°C) **(Section 9.2)**

$$V = V_0\left(1 + \frac{t}{273.15°\text{C}}\right)$$ **(Section 9.2)**

$T \text{ (Kelvin)} = 273.15 + t \text{ (Celsius)}$ **(Section 9.2)**

$V \propto T$ (fixed temperature and fixed amount of gas) **(Section 9.2)**

$$V = R\frac{nT}{P} \quad \text{or} \quad PV = nRT$$ (ideal gas) **(Section 9.3)**

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$ (ideal gas) **(Section 9.3)**

$$P_{\text{tot}} = P_{\text{A}} + P_{\text{B}} + P_{\text{C}} + \cdots = \qquad \text{(Section 9.4)}$$

$$(n_{\text{A}} + n_{\text{B}} + n_{\text{C}} + \cdots)\frac{RT}{V} = n_{\text{tot}}\frac{RT}{V} \qquad \text{(Section 9.4)}$$

$$P_{\text{A}} = X_{\text{A}}P_{\text{tot}} \qquad \text{(Section 9.4)}$$

$$PV = \tfrac{1}{3}Nm\overline{u^2} \qquad \text{(Section 9.5)}$$

$$\tfrac{1}{3}\mathrm{N_A}m\overline{u^2} = RT \qquad \text{(Section 9.5)}$$

$$\overline{\mathrm{E}} = \mathrm{N_A}m\overline{u^2} = \tfrac{3}{2} \times (\tfrac{1}{3}\mathrm{N_A}m\overline{u^2}) = \tfrac{3}{2}RT \qquad \text{(Section 9.5)}$$

$$\overline{\varepsilon} = \frac{3}{2}k_{\text{B}}T \qquad \text{(Section 9.5)}$$

$$\overline{u^2} = \frac{3RT}{\mathcal{M}} \qquad \text{(Section 9.5)}$$

$$u_{\text{rms}} = \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{\mathcal{M}}} \qquad \text{(Section 9.5)}$$

$$f(u) = 4\pi\left(\frac{m}{2\pi k_{\text{B}}T}\right)^{3/2}u^2\exp(-mu^2/2k_{\text{B}}T) \qquad \text{(Section 9.5)}$$

$$u_{\text{mp}} = \sqrt{\frac{2k_{\text{B}}T}{m}} = \sqrt{\frac{2RT}{\mathcal{M}}} \qquad \text{(Section 9.5)}$$

$$\overline{u} = \sqrt{\frac{8k_{\text{B}}T}{\pi m}} = \sqrt{\frac{8RT}{\pi\mathcal{M}}} \qquad \text{(Section 9.5)}$$

$$P(n) = C\exp(-E_n/k_{\text{B}}T) \qquad \text{(Section 9.6)}$$

$$\frac{P(n)}{P(0)} = \frac{C\exp(-E_n/k_{\text{B}}T)}{C\exp(-E_0/k_{\text{B}}T)} = \exp(-[E_n - E_0]/k_{\text{B}}T) \qquad \text{(Section 9.6)}$$

$$z = \frac{PV}{nRT} \qquad \text{(Section 9.7)}$$

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$

$$P = \frac{nRT}{V - nb} - a\frac{n^2}{V^2} \qquad \text{(Section 9.7)}$$

$$V_{\text{LJ}}(R) = 4\varepsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right] \qquad \text{(Section 9.7)}$$

$$Z_w \propto \frac{1}{4}\frac{N}{V}\overline{u}A = \frac{1}{4}\frac{N}{V}\sqrt{\frac{8RT}{\pi\mathcal{M}}}A \qquad \text{(Section 9.8)}$$

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \frac{\dfrac{1}{4}\dfrac{\mathrm{N_A}}{V}\sqrt{\dfrac{8RT}{\pi\mathcal{M}_{\text{A}}}}A}{\dfrac{1}{4}\dfrac{\mathrm{N_B}}{V}\sqrt{\dfrac{8RT}{\pi\mathcal{M}_{\text{B}}}}A} = \frac{\mathrm{N_A}}{\mathrm{N_B}}\sqrt{\frac{\mathcal{M}_{\text{B}}}{\mathcal{M}_{\text{A}}}} \qquad \text{(Section 9.8)}$$

$$Z_1 = 4\frac{N}{V}d^2\sqrt{\frac{\pi RT}{\mathcal{M}}} \qquad \text{(Section 9.8)}$$

$$\lambda = \overline{u}Z_1^{-1} = \frac{\overline{u}}{\sqrt{2}(N/V)\pi d^2\overline{u}} = \frac{1}{\sqrt{2}\pi d^2 N/V} \qquad \text{(Section 9.8)}$$

$$\overline{\Delta r^2} = 6Dt \qquad \text{(Section 9.8)}$$

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

The Chemistry of Gases

1. Solid ammonium hydrosulfide (NH_4HS) decomposes entirely to gases when it is heated. Write a chemical equation representing this change.

2. Solid ammonium carbamate ($NH_4CO_2NH_2$) decomposes entirely to gases when it is heated. Write a chemical equation representing this change.

3. Ammonia (NH_3) is an important and useful gas. Suggest a way to generate it from ammonium bromide (NH_4Br). Include a balanced chemical equation.

4. Hydrogen cyanide (HCN) is a poisonous gas. Explain why solutions of potassium cyanide (KCN) should never be acidified. Include a balanced chemical equation.

Pressure and Temperature of Gases

5. Suppose a barometer were designed using water (with a density of 1.00 g cm^{-3}) rather than mercury as its fluid. What would be the height of the column of water balancing 1.00 atm pressure?

6. A vessel that contains a gas has two pressure gauges attached to it. One contains liquid mercury, and the other an oil such as dibutylphthalate. The difference in levels of mercury in the two arms of the mercury gauge is observed to be 9.50 cm. Given

$$\text{density of mercury} = 13.60 \text{ g cm}^{-3}$$

$$\text{density of oil} = 1.045 \text{ g cm}^{-3}$$

$$\text{acceleration due to gravity} = 9.806 \text{ m s}^{-2}$$

(a) What is the pressure of the gas?
(b) What is the difference in height of the oil in the two arms of the oil pressure gauge?

7. Calcium dissolved in the ocean is used by marine organisms to form $CaCO_3(s)$ in skeletons and shells. When the organisms die, their remains fall to the bottom. The amount of calcium carbonate that can be dissolved in seawater depends on the pressure. At great depths, where the pressure exceeds about 414 atm, the shells slowly redissolve. This reaction prevents all the Earth's calcium from being tied up as insoluble $CaCO_3(s)$ at the bottom of the sea. Estimate the depth (in feet) of water that exerts a pressure great enough to dissolve seashells.

8. Suppose that the atmosphere were perfectly uniform, with a density throughout equal to that of air at 0°C, 1.3 g L^{-1}. Calculate the thickness of such an atmosphere that would cause a pressure of exactly 1 standard atm at the Earth's surface.

9. The "critical pressure" of mercury is 172.00 MPa. Above this pressure mercury cannot be liquefied, no matter what the temperature. Express this pressure in atmospheres and in bars (1 bar = 10^5 Pa).

10. Experimental studies of solid surfaces and the chemical reactions that occur on them require very low gas pressures to avoid surface contamination. High-vacuum apparatus for such experiments can routinely reach pressures of 5×10^{-10} torr. Express this pressure in atmospheres and in pascals.

11. Some nitrogen is held in a 2.00-L tank at a pressure of 3.00 atm. The tank is connected to a 5.00-L tank that is completely empty (evacuated), and a valve is opened to connect the two tanks. No temperature change occurs in the process. Determine the total pressure in this two-tank system after the nitrogen stops flowing.

12. The Stirling engine, a heat engine invented by a Scottish minister, has been considered for use in automobile engines because of its efficiency. In such an engine, a gas goes through a four-step cycle: (1) expansion at constant T, (2) cooling at constant V, (3) compression at constant T to its original volume, and (4) heating at constant V to its original temperature. Suppose the gas starts at a pressure of 1.23 atm and the volume of the gas changes from 0.350 to 1.31 L during its expansion at constant T. Calculate the pressure of the gas at the end of this step in the cycle.

13. The absolute temperature of a 4.00-L sample of gas doubles at constant pressure. Determine the volume of the gas after this change.

14. The Celsius temperature of a 4.00-L sample of gas doubles from 20.0°C to 40.0°C at constant pressure. Determine the volume of the gas after this change.

15. The gill is an obscure unit of volume. If some $H_2(g)$ has a volume of 17.4 gills at 100°F, what volume would it have if the temperature were reduced to 0°F, assuming that its pressure stayed constant?

16. A gas originally at a temperature of 26.5°C is cooled at constant pressure. Its volume decreases from 5.40 L to 5.26 L. Determine its new temperature in degrees Celsius.

17. Calcium carbide (CaC_2) reacts with water to produce acetylene (C_2H_2), according to the following equation:

$$CaC_2(s) + 2\,H_2O(\ell) \longrightarrow Ca(OH)_2(s) + C_2H_2(g)$$

A certain mass of CaC_2 reacts completely with water to give 64.5 L C_2H_2 at 50°C and $P = 1.00$ atm. If the same mass of CaC_2 reacts completely at 400°C and $P = 1.00$ atm, what volume of C_2H_2 will be collected at the higher temperature?

18. A convenient laboratory source for high purity oxygen is the decomposition of potassium permanganate at 230°C:

$$2\,KMnO_4(s) \longrightarrow K_2MnO_4(s) + MnO_2(s) + O_2(g)$$

Suppose 3.41 L oxygen is needed at atmospheric pressure and a temperature of 20°C. What volume of oxygen should be collected at 230°C and the same pressure to give this volume when cooled?

The Ideal Gas Law

19. A bicycle tire is inflated to a gauge pressure of 30.0 psi at a temperature of $t = 0$°C. What will its gauge pressure be at 32°C if the tire is considered nonexpandable? (**Note:** The gauge pressure is the *difference* between the tire pressure and atmospheric pressure, 14.7 psi.)

20. The pressure of a poisonous gas inside a sealed container is 1.47 atm at 20°C. If the barometric pressure is 0.96 atm, to what temperature (in degrees Celsius) must the container and its contents be cooled so that the container can be opened with no risk for gas spurting out?

21. A 20.6-L sample of "pure" air is collected in Greenland at a temperature of −20.0°C and a pressure of 1.01 atm and is forced into a 1.05-L bottle for shipment to Europe for analysis.

(a) Compute the pressure inside the bottle just after it is filled.

(b) Compute the pressure inside the bottle as it is opened in the 21.0°C comfort of the European laboratory.

22. Iodine heptafluoride (IF_7) can be made at elevated temperatures by the following reaction:

$$I_2(g) + 7\ F_2(g) \longrightarrow 2\ IF_7(g)$$

Suppose 63.6 L gaseous IF_7 is made by this reaction at 300°C and a pressure of 0.459 atm. Calculate the volume this gas will occupy if heated to 400°C at a pressure of 0.980 atm.

23. According to a reference handbook, "The weight of one liter of $H_2Te(g)$ is 6.234 g." Why is this information nearly valueless? Assume that $H_2Te(g)$ is an ideal gas, and calculate the temperature (in degrees Celsius) at which this statement is true if the pressure is 1.00 atm.

24. A scuba diver's tank contains 0.30 kg oxygen (O_2) compressed into a volume of 2.32 L.

(a) Use the ideal gas law to estimate the gas pressure inside the tank at 5°C, and express it in atmospheres and in pounds per square inch.

(b) What volume would this oxygen occupy at 30°C and a pressure of 0.98 atm?

25. Hydrogen is produced by the complete reaction of 6.24 g sodium with an excess of gaseous hydrogen chloride.

(a) Write a balanced chemical equation for the reaction that occurs.

(b) How many liters of hydrogen will be produced at a temperature of 50.0°C and a pressure of 0.850 atm?

26. Aluminum reacts with excess aqueous hydrochloric acid to produce hydrogen.

(a) Write a balanced chemical equation for the reaction. (*Hint:* Water-soluble $AlCl_3$ is the stable chloride of aluminum.)

(b) Calculate the mass of pure aluminum that will furnish 10.0 L hydrogen at a pressure of 0.750 atm and a temperature of 30.0°C.

27. The classic method for manufacturing hydrogen chloride, which is still in use today to a small extent, is the reaction of sodium chloride with excess sulfuric acid at elevated temperatures. The overall equation for this process is

$$NaCl(s) + H_2SO_4(\ell) \longrightarrow NaHSO_4(s) + HCl(g)$$

What volume of hydrogen chloride is produced from 2500 kg sodium chloride at 550°C and a pressure of 0.97 atm?

28. In 1783, the French physicist Jacques Charles supervised and took part in the first human flight in a hydrogen balloon. Such balloons rely on the low density of hydrogen relative to air for their buoyancy. In Charles's balloon ascent, the hydrogen was produced (together with iron(II) sulfate) from the action of aqueous sulfuric acid on iron filings.

(a) Write a balanced chemical equation for this reaction.

(b) What volume of hydrogen is produced at 300 K and a pressure of 1.0 atm when 300 kg sulfuric acid is consumed in this reaction?

(c) What would be the radius of a spherical balloon filled by the gas in part (b)?

29. Potassium chlorate decomposes when heated, giving oxygen and potassium chloride:

$$2\ KClO_3(s) \longrightarrow 2\ KCl(s) + 3\ O_2(g)$$

A test tube holding 87.6 g $KClO_3$ is heated, and the reaction goes to completion. What volume of O_2 will be evolved if it is collected at a pressure of 1.04 atm and a temperature of 13.2°C?

30. Elemental chlorine was first produced by Carl Wilhelm Scheele in 1774 using the reaction of pyrolusite (MnO_2) with sulfuric acid and sodium chloride:

$$4\ NaCl(s) + 2\ H_2SO_4(\ell) + MnO_2(s) \longrightarrow 2\ Na_2SO_4(s) + MnCl_2(s) + 2\ H_2O(\ell) + Cl_2(g)$$

Calculate the minimum mass of MnO_2 required to generate 5.32 L gaseous chlorine, measured at a pressure of 0.953 atm and a temperature of 33°C.

31. Elemental sulfur can be recovered from gaseous hydrogen sulfide (H_2S) through the following reaction:

$$2\ H_2S(g) + SO_2(g) \longrightarrow 3\ S(s) + 2\ H_2O(\ell)$$

(a) What volume of H_2S (in liters at 0°C and 1.00 atm) is required to produce 2.00 kg (2000 g) sulfur by this process?

(b) What minimum mass and volume (at 0°C and 1.00 atm) of SO_2 are required to produce 2.00 kg sulfur by this reaction?

32. When ozone (O_3) is placed in contact with dry, powdered KOH at −15°C, the red-brown solid potassium ozonide (KO_3) forms, according to the following balanced equation:

$$5\ O_3(g) + 2\ KOH(s) \longrightarrow 2\ KO_3(s) + 5\ O_2(g) + H_2O(s)$$

Calculate the volume of ozone needed (at a pressure of 0.134 atm and −15°C) to produce 4.69 g KO_3.

Mixtures of Gases

33. Sulfur dioxide reacts with oxygen in the presence of platinum to give sulfur trioxide:

$$2\ SO_2(g) + O_2(g) \longrightarrow 2\ SO_3(g)$$

Suppose that at one stage in the reaction, 26.0 mol SO_2, 83.0 mol O_2, and 17.0 mol SO_3 are present in the reaction vessel at a total pressure of 0.950 atm. Calculate the mole fraction of SO_3 and its partial pressure.

34. The synthesis of ammonia from the elements is conducted at high pressures and temperatures:

$$N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g)$$

Suppose that at one stage in the reaction, 13 mol NH_3, 31 mol N_2, and 93 mol H_2 are present in the reaction vessel at a total pressure of 210 atm. Calculate the mole fraction of NH_3 and its partial pressure.

35. The atmospheric pressure at the surface of Mars is 5.92×10^{-3} atm. The Martian atmosphere is 95.3% CO_2 and 2.7% N_2 by volume, with small amounts of other gases also present. Compute the mole fraction and partial pressure of N_2 in the atmosphere of Mars.

36. The atmospheric pressure at the surface of Venus is 90.8 atm. The Venusian atmosphere is 96.5% CO_2 and 3.5% N_2 by volume, with small amounts of other gases also present. Compute the mole fraction and partial pressure of N_2 in the atmosphere of Venus.

37. A gas mixture at room temperature contains 10.0 mol CO and 12.5 mol O_2.

(a) Compute the mole fraction of CO in the mixture.

(b) The mixture is then heated, and the CO starts to react with the O_2 to give CO_2:

$$\mathrm{CO}(g) + \frac{1}{2}\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$$

At a certain point in the heating, 3.0 mol CO_2 is present. Determine the mole fraction of CO in the new mixture.

38. A gas mixture contains 4.5 mol Br_2 and 33.1 mol F_2.

(a) Compute the mole fraction of Br_2 in the mixture.

(b) The mixture is heated above 150°C and starts to react to give BrF_5:

$$\mathrm{Br_2}(g) + 5\,\mathrm{F_2}(g) \longrightarrow 2\,\mathrm{BrF_5}(g)$$

At a certain point in the reaction, 2.2 mol BrF_5 is present. Determine the mole fraction of Br_2 in the mixture at that point.

39. The partial pressure of water vapor in saturated air at 20°C is 0.0230 atm.

(a) How many molecules of water are in 1.00 cm^3 of saturated air at 20°C?

(b) What volume of saturated air at 20°C contains 0.500 mol water?

40. The partial pressure of oxygen in a mixture of oxygen and hydrogen is 0.200 atm, and that of hydrogen is 0.800 atm.

(a) How many molecules of oxygen are in a 1.500-L container of this mixture at 40°C?

(b) If a spark is introduced into the container, how many grams of water will be produced?

The Kinetic Theory of Gases

41. (a) Compute the root-mean-square speed of H_2 molecules in hydrogen at a temperature of 300 K.

(b) Repeat the calculation for SF_6 molecules in gaseous sulfur hexafluoride at 300 K.

42. Researchers recently reported the first optical atomic trap. In this device, beams of laser light replace the physical walls of conventional containers. The laser beams are tightly focused. They briefly (for 0.5 s) exert enough pressure to confine 500 sodium atoms in a volume of 1.0×10^{-15} m^3. The temperature of this gas is 0.00024 K, the lowest temperature ever reached for a gas. Compute the root-mean-square speed of the atoms in this confinement.

43. Compare the root-mean-square speed of helium atoms near the surface of the sun, where the temperature is approximately 6000 K, with that of helium atoms in an interstellar cloud, where the temperature is 100 K.

44. The "escape velocity" necessary for objects to leave the gravitational field of the Earth is 11.2 km s^{-1}. Calculate the ratio of the escape velocity to the root-mean-square speed of helium, argon, and xenon atoms at 2000 K. Does your result help explain the low abundance of the light gas helium in the atmosphere? Explain.

45. Chlorine dioxide (ClO_2) is used for bleaching wood pulp. In a gaseous sample held at thermal equilibrium at a particular temperature, 35.0% of the molecules have speeds exceeding 400 m s^{-1}. If the sample is heated slightly, will the percentage of molecules with speeds in excess of 400 m s^{-1} then be greater than or less than 35%? Explain.

46. The ClO_2 described in Problem 45 is heated further until it explodes, yielding Cl_2, O_2, and other gaseous products. The mixture is then cooled until the original temperature is reached. Is the percentage of *chlorine* molecules with speeds in excess of 400 m s^{-1} greater than or less than 35%? Explain.

Distribution of Energy among Molecules

47. Calculate the relative populations of two energy levels separated by 0.4×10^{-21} J in a gas at temperature 25°C.

48. Calculate the relative populations of two energy levels separated by 40×10^{-21} J in a gas at temperature 25°C.

49. Estimate the ratio of the number of molecules in the first excited vibrational state of the molecule N_2 to the number in the ground state, at a temperature of 450 K. The vibrational frequency of N_2 is 7.07×10^{13} s^{-1}.

50. The vibrational frequency of the ICl molecule is 1.15×10^{13} s^{-1}. For every million (1.00×10^6) molecules in the ground vibrational state, how many will be in the first excited vibrational state at a temperature of 300 K?

51. The force constant for HF is 966 N m^{-1}. Using the harmonic oscillator model, calculate the relative population of the first excited state and the ground state at 300 K.

52. The force constant for HBr is 412 N m^{-1}. Using the harmonic oscillator model, calculate the relative population of the first excited state and the ground state at 300 K.

53. The Boltzmann distribution describes the relative population of molecules at different altitudes in a column of air above the surface of the earth due to the differences in their gravitational potential energy at these altitudes. The most convenient form of this distribution—called the barometric equation—relates the pressure P_h in the column at altitude h to its value P_0 at the surface of the earth as $P_h = P_0 \exp[-\mathcal{M}gh/RT]$, where $\mathcal{M}$ is the molar mass of the gas and g is the acceleration of gravity. Calculate the pressure at an altitude of 1 km for a gas with average molar mass 29 g mol^{-1} when the temperature is 298 K and the pressure at the surface of the earth is 1 atm.

54. If we assume that the atmosphere of the earth is an ideal gas mixture, then each component is described by a separate barometric equation. This model predicts that the concentrations of heavier molecules, and therefore their partial pressures, decrease faster than for lighter molecules as the altitude increases. Assume the ratio of partial pressure of nitrogen to oxygen is 4 at the surface of the earth, corresponding to 80% nitrogen by moles, and assume the temperature throughout the column in 25 C. Calculate the value of P_{N_2}/P_{O_2} at the altitude of 10 km.

Real Gases: Intermolecular Forces

55. Oxygen is supplied to hospitals and chemical laboratories under pressure in large steel cylinders. Typically, such cylinders have an internal volume of 28.0 L and contain 6.80 kg oxygen. Use the van der Waals equation to estimate the pressure inside such cylinders at 20°C in atmospheres and in pounds per square inch.

56. Steam at high pressures and temperatures is used to generate electrical power in utility plants. A large utility boiler has a volume of 2500 m^3 and contains 140 metric tons (1 metric ton = 10^3 kg) of steam at a temperature of 540°C. Use the van der Waals equation to estimate the pressure of the steam under these conditions, in atmospheres and in pounds per square inch.

57. Using (a) the ideal gas law and (b) the van der Waals equation, calculate the pressure exerted by 50.0 g carbon dioxide in a 1.00-L vessel at 25°C. Do attractive or repulsive forces dominate?

58. When 60.0 g methane (CH_4) is placed in a 1.00-L vessel, the pressure is measured to be 130 atm. Calculate the temperature of the gas using (a) the ideal gas law and (b) the van der Waals equation. Do attractive or repulsive forces dominate?

Molecular Collisions and Rate Processes

59. A spherical bulb with a volume of 500 cm^3 is evacuated to a negligibly small residual gas pressure and then closed off. One hour later, the pressure in the vessel is found to be 1.00×10^{-7} atm because the bulb has a tiny hole in it. Assume that the surroundings are at atmospheric pressure, T = 300 K, and the average molar mass of molecules in the atmosphere is 28.8 g mol^{-1}. Calculate the radius of the hole in the vessel wall, assuming it to be circular.

60. A 200-cm^3 vessel contains hydrogen gas at a temperature of 25°C and a pressure of 0.990 atm. Unfortunately, the vessel has a tiny hole in its wall, and over a period of 1 hour, the pressure drops to 0.989 atm. What is the radius of the hole (assumed to be circular)?

61. Methane (CH_4) effuses through a small opening in the side of a container at the rate of 1.30×10^{-8} mol s^{-1}. An unknown gas effuses through the same opening at the rate of 5.42×10^{-9} mol s^{-1} when maintained at the same temperature and pressure as the methane. Determine the molar mass of the unknown gas.

62. Equal chemical amounts of two gases, fluorine and bromine pentafluoride, are mixed. Determine the ratio of the rates of effusion of the two gases through a small opening in their container.

63. Calculate the theoretical number of stages that would be needed to enrich ^{235}U to 95% purity by means of the barrier diffusion process, using $^{235}UF_6$ and $^{238}UF_6$ as the gaseous compounds. The natural abundance of ^{238}U is 99.27%, and that of ^{235}U is 0.72%. Take the relative atomic masses of ^{235}U and ^{238}U to be 235.04 and 238.05, respectively.

64. A mixture of H_2 and He at 300 K effuses from a tiny hole in the vessel that contains it. What is the mole fraction of H_2 in the original gas mixture if 3.00 times as many He atoms as H_2 molecules escape from the orifice in unit time? If the same mixture is to be separated by a barrier-diffusion process, how many stages are necessary to achieve H_2 of 99.9% purity?

65. At what pressure does the mean free path of krypton (Kr) atoms ($d = 3.16 \times 10^{-10}$ m) become comparable with the diameter of the 1-L spherical vessel that contains them at 300 K? Calculate the diffusion constant at this pressure.

66. At what pressure does the mean free path of Kr atoms ($d = 3.16 \times 10^{-10}$ m) become comparable with the diameter of a Kr atom if T = 300 K? Calculate the diffusion constant at this pressure. Assume that Kr obeys the ideal gas law even at these high pressures.

ADDITIONAL PROBLEMS

67. The Earth is approximately a sphere of radius 6370 km. Taking the average barometric pressure on the Earth's surface to be 730 mm Hg, estimate the total mass of the Earth's atmosphere.

* **68.** After a flood fills a basement to a depth of 9.0 feet and completely saturates the surrounding earth, the owner buys an electric pump and quickly pumps the water out of the basement. Suddenly, a basement wall collapses, the structure is severely damaged, and mud oozes in. Explain this event by estimating the difference between the outside pressure at the base of the basement walls and the pressure inside the drained basement. Assume that the density of the mud is 4.9 g cm^{-3}. Report the answer both in atmospheres and in pounds per square inch.

69. The density of mercury is 13.5955 g cm^{-3} at 0.0°C, but only 13.5094 g cm^{-3} at 35°C. Suppose that a mercury barometer is read on a hot summer day when the temperature is 35°C. The column of mercury is 760.0 mm long. Correct for the expansion of the mercury and compute the true pressure in atmospheres.

70. When a gas is cooled at constant pressure, the volume decreases according to the following equation:

$$V = 209.4 \text{ L} + \left(0.456 \frac{\text{L}}{°\text{F}}\right) \times t_F$$

where t_F is the temperature in degrees Fahrenheit. From this relationship, estimate the absolute zero of temperature in degrees Fahrenheit.

71. Amonton's law relates pressure to absolute temperature. Consider the ideal gas law and then write a statement of Amonton's law in a form that is analogous to the statements of Charles's law and Boyle's law in the text.

72. The density of a certain gas is 2.94 g L^{-1} at 50°C and P = 1.00 atm. What is its density at 150°C? Calculate the molar mass of the gas, assuming it obeys the ideal gas law.

73. A lighter-than-air balloon contains 1005 mol helium at 1.00 atm and 25.0°C.

(a) Compute the difference between the mass of the helium it contains and the mass of the air it displaces, assuming the molar mass of air to be 29.0 g mol^{-1}.

(b) The balloon now ascends to an altitude of 10 miles, where the temperature is −80.0°C. The walls of the balloon are elastic enough that the pressure inside it equals the pressure outside. Repeat the calculation of part (a).

74. Baseball reporters say that long fly balls that would have carried for home runs in July "die" in the cool air of October and are caught. The idea behind this observation is that a baseball carries better when the air is less dense. Dry air is a mixture of gases with an effective molar mass of 29.0 g mol^{-1}.

(a) Compute the density of dry air on a July day when the temperature is 95.0°F and the pressure is 1.00 atm.

(b) Compute the density of dry air on an October evening when the temperature is 50.0°F and the pressure is 1.00 atm.

(c) Suppose that the humidity on the July day is 100%; thus, the air is saturated with water vapor. Is the density of this hot, moist air less than, equal to, or greater than the density of the hot, dry air computed in part (a)? In other terms, does high humidity favor the home run?

75. Sulfuric acid reacts with sodium chloride to produce gaseous hydrogen chloride according to the following reaction:

$$NaCl(s) + H_2SO_4(\ell) \longrightarrow NaHSO_4(s) + HCl(g)$$

A 10.0-kg mass of NaCl reacts completely with sulfuric acid to give a certain volume of $HCl(g)$ at 50°C and P = 1.00 atm. If the same volume of hydrogen chloride is collected at 500°C and P = 1.00 atm, what mass of NaCl has reacted?

76. Exactly 1.0 lb Hydrone, an alloy of sodium with lead, yields (at 0.0°C and 1.00 atm) 2.6 ft^3 of hydrogen when it is treated with water. All the sodium reacts according to the following reaction:

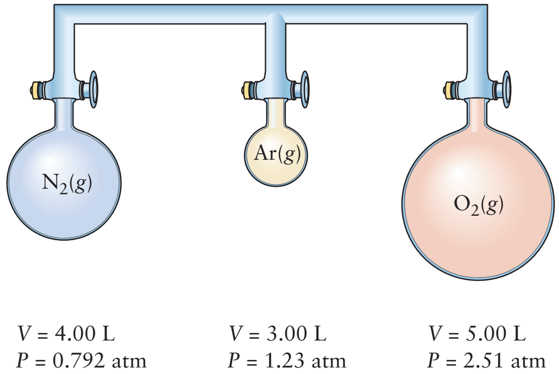
$$2\ Na_{\text{in alloy}} + 2\ H_2O(\ell) \longrightarrow 2\ NaOH(aq) + H_2(g)$$

and the lead does not react with water. Compute the percentage by mass of sodium in the alloy.

77. A sample of limestone (calcium carbonate, $CaCO_3$) is heated at 950 K until it is completely converted to calcium oxide (CaO) and CO_2. The CaO is then all converted to calcium hydroxide by addition of water, yielding 8.47 kg of solid $Ca(OH)_2$. Calculate the volume of CO_2 produced in the first step, assuming it to be an ideal gas at 950 K and a pressure of 0.976 atm.

78. A gas exerts a pressure of 0.740 atm in a certain container. Suddenly, a chemical change occurs that consumes half of the molecules originally present and forms two new molecules for every three consumed. Determine the new pressure in the container if the volume of the container and the temperature are unchanged.

79. The following arrangement of flasks is set up. Assuming no temperature change, determine the final pressure inside the system after all stopcocks are opened. The connecting tube has zero volume.



* **80.** A mixture of $CS_2(g)$ and excess $O_2(g)$ in a 10.0-L reaction vessel at 100.0°C is under a pressure of 3.00 atm. When the mixture is ignited by a spark, it explodes. The vessel successfully contains the explosion, in which all of the $CS_2(g)$ reacts to give $CO_2(g)$ and $SO_2(g)$. The vessel is cooled back to its original temperature of 100.0°C, and the pressure of the mixture of the two product gases and the unreacted $O_2(g)$ is found to be 2.40 atm. Calculate the mass (in grams) of $CS_2(g)$ originally present.

81. Acetylene reacts with hydrogen in the presence of a catalyst to form ethane according to the following reaction:

$$C_2H_2(g) + 2\ H_2(g) \longrightarrow C_2H_6(g)$$

The pressure of a mixture of acetylene and an excess of hydrogen decreases from 0.100 to 0.042 atm in a vessel of a given volume after the catalyst is introduced, and the temperature is restored to its initial value after the reaction reaches completion. What was the mole fraction of acetylene in the original mixture?

82. Refer to the atomic trap described in Problem 42.

(a) Assume ideal gas behavior to compute the pressure exerted on the "walls" of the optical bottle in this experiment.

(b) In this gas, the mean free path (the average distance traveled by the sodium atoms between collisions) is 3.9 m. Compare this with the mean free path of the atoms in gaseous sodium at room conditions.

83. Deuterium (^2H), when heated to sufficiently high temperature, undergoes a nuclear fusion reaction that results in the production of helium. The reaction proceeds rapidly at a temperature, T, at which the average kinetic energy of the deuterium atoms is 8×10^{-16} J. (At this temperature, deuterium molecules dissociate completely into deuterium atoms.)

(a) Calculate T in kelvins (atomic mass of ^2H = 2.015).

(b) For the fusion reaction to occur with ordinary H atoms, the average energy of the atoms must be about 32×10^{-16} J. By what factor does the average speed of the ^1H atoms differ from that of the ^2H atoms of part (a)?

84. Molecules of oxygen of the following isotopic composition are separated in an oxygen enrichment plant: $^{16}O^{16}O$, $^{16}O^{17}O$, $^{16}O^{18}O$, $^{17}O^{17}O$, $^{17}O^{18}O$, $^{18}O^{18}O$.

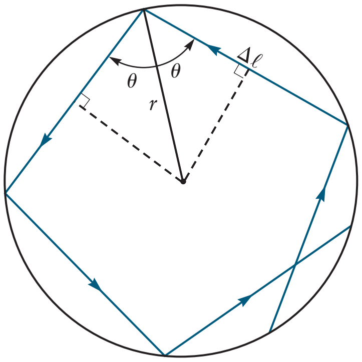
(a) Compare the average translational kinetic energy of the lightest and heaviest molecular oxygen species at 200°C and at 400°C.

(b) Compare the average speeds of the lightest and heaviest molecular oxygen species at the same two temperatures.

*** 85.** What is the probability that an O_2 molecule in a sample of oxygen at 300 K has a speed between 5.00×10^2 and 5.10×10^2 m s^{-1}? (*Hint:* Try approximating the area under the Maxwell–Boltzmann distribution by small rectangles.)

*** 86.** Molecules in a spherical container make wall collisions in a great circle plane of the sphere. All paths traveled between collisions are equal in length.

(a) Relate the path length $\Delta\ell$ to the angle θ and the sphere radius r.



(b) Express the component of the molecular momentum transferred to the wall in a collision in terms of the molecular mass m, the speed u, and the angle θ.

(c) Using parts (a) and (b), calculate the average force exerted on the wall by one molecule.

(d) Derive the relation $PV = PV = \frac{1}{3}N m \overline{u^2}$ for a spherical container. This is the same relation found for a rectangular box in Section 9.5.

*** 87.** The van der Waals constant b is related to the volume excluded per mole of molecules, so it should be proportional to $N_A\sigma^3$, where σ is the distance parameter in the Lennard–Jones potential.

(a) Make a plot of b against $N_A\sigma^3$ for Ar, H_2, CH_4, N_2, and O_2, using data from Tables 9.3 and 9.4. Do you see an overall correlation between the two?

(b) The van der Waals constant a has dimensions of pressure times the square of the molar volume. Rewrite the units of a in terms of energy, length, and number of moles, and suggest a relation between a and some combination of the constants ε, σ, and N_A. Make a plot of a against this combination of constants for the gases of part (a). Do you see an overall correlation in this case?

*** 88.** Take the derivative of the Lennard–Jones potential to express the force exerted on one atom by another for the distance R between them. Calculate the forces (in joules per meter) on a pair of interacting argon atoms at distances of 3.0, 3.4, 3.8, and 4.2×10^{-10} m. Is the force attractive or repulsive at each of these distances?

89. A vessel with a small hole in its wall is filled with oxygen to a pressure of 1.00 atm at 25°C. In a 1.00-minute period, 3.25 g oxygen effuses out through the hole into a vacuum. The vessel is evacuated and filled with an unknown gas at the same pressure and volume. In this case, 5.39 g of the unknown gas effuses in 1.00 minute. Calculate the molar mass of the unknown gas.

90. A cylindrical storage tank for natural gas (mostly methane, CH_4) with a 20-ft radius and a 50-ft height is filled to a pressure of 2000 psi at 20°C. A small leak of 1.0-mm^2 area develops at one of the welds. Calculate the mass of CH_4 (in grams) that leaks out of the tank in one day. What fraction of the total gas escapes per day?

91. A thermos bottle (Dewar vessel) has an evacuated space between its inner and outer walls to diminish the rate of transfer of thermal energy to or from the bottle's contents. For good insulation, the mean free path of the residual gas (air; average molecular mass = 29) should be at least 10 times the distance between the inner and outer walls, which is about 1.0 cm. What should be the maximum residual gas pressure in the evacuated space if $T = 300$ K? Take an average diameter of $d = 3.1 \times 10^{-10}$ m for the molecules in the air.

92. A tanker truck carrying liquid ammonia overturns, releasing ammonia vapor into the air.

(a) Approximating ammonia, oxygen, and nitrogen as spheres of equal diameter (3×10^{-10} m), estimate the diffusion constant of ammonia in air at atmospheric pressure and 20°C.

(b) Calculate the time required for a 100-m root-mean-square displacement of ammonia from the truck, and express this time in everyday units (seconds, minutes, hours, days, or years). The actual time for the ammonia to travel this distance is far shorter because of the existence of air currents (even when there is no wind).

93. Molecules of UF_6 are approximately 175 times more massive than H_2 molecules; however, Avogadro's number of H_2 molecules confined at a set temperature exert the same pressure on the walls of the container as the same number of UF_6 molecules. Explain how this is possible.

94. The number density of atoms (chiefly hydrogen) in interstellar space is about 10 per cubic centimeter, and the temperature is about 100 K.

(a) Calculate the pressure of the gas in interstellar space, and express it in atmospheres.

(b) Under these conditions, an atom of hydrogen collides with another atom once every 1×10^9 seconds (that is, once every 30 years). By using the root-mean-square speed, estimate the distance traveled by a H atom between collisions. Compare this distance with the distance from the Earth to the Sun (150 million km).

95. A sample of 2.00 mol argon is confined at low pressure in a volume at a temperature of 50°C. Describe quantitatively the effects of each of the following changes on the pressure, the average energy per atom in the gas, the root-mean-square speed, the rate of collisions with a given area of wall, the frequency of Ar–Ar collisions, and the mean free path:

(a) The temperature is decreased to −50°C.

(b) The volume is doubled.

(c) The amount of argon is increased to 3.00 mol.

96. By assuming that the collision diameter of a CH_4 molecule is given by its Lennard–Jones σ parameter (see Table 9.4), estimate the rate at which methane molecules collide with one another at 25°C and a pressure of (a) 1.00 atm and (b) 1.0×10^{-7} atm.

CUMULATIVE PROBLEMS

97. A gaseous hydrocarbon, in a volume of 25.4 L at 400 K and a pressure of 3.40 atm, reacts in an excess of oxygen to give 47.4 g H_2O and 231.6 g CO_2. Determine the molecular formula of the hydrocarbon.

98. A sample of a gaseous binary compound of boron and chlorine weighing 2.842 g occupies 0.153 L at 0°C and 1.00 atm pressure. This sample is decomposed to give solid boron and gaseous chlorine (Cl_2). The chlorine occupies 0.688 L at the same temperature and pressure. Determine the molecular formula of the compound.

99. A mixture of calcium carbonate, $CaCO_3$, and barium carbonate, $BaCO_3$, weighing 5.40 g reacts fully with hydrochloric acid, HCl(*aq*), to generate 1.39 L $CO_2(g)$, measured at 50°C and 0.904 atm pressure. Calculate the percentages by mass of $CaCO_3$ and $BaCO_3$ in the original mixture.

100. A solid sample of Rb_2SO_3 weighing 6.24 g reacts with 1.38 L gaseous HBr, measured at 75°C and 0.953 atm pressure. The solid RbBr, extracted from the reaction mixture and purified, has a mass of 7.32 g.

(a) What is the limiting reactant?

(b) What is the theoretical yield of RbBr, assuming complete reaction?

(c) What is the actual percentage yield of product?

CHAPTER 10

Solids, Liquids, and Phase Transitions

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Solid iodine is converted directly to a vapor (sublimes) when warmed. Here, purple iodine vapor is redeposited as a solid on the cooler upper surfaces of the vessel.

The bulk properties of gases, liquids, and solids—molar volume, density, compressibility, and thermal expansion, among others—differ widely, often by orders of magnitude. All of these properties depend on the temperature and pressure and describe the response of the system to changes in those variables. The average separation between molecules, and the nature of the intermolecular forces present, determine the properties of the bulk. The local structure—the arrangement of atoms or molecules on the nanometer length scale—is the key microscopic feature that distinguishes the three states of matter from one another and ultimately determines the differences in their bulk properties.

We begin with a brief survey of several important bulk properties and discuss how the number density of molecules and the strength of intermolecular forces rationalize the properties observed. Then, we describe the various kinds of intermolecular forces and show how these forces originate in the structures of molecules. Finally, we survey the transitions between the states of matter as consequences of intermolecular forces. In the previous chapter we derived the ideal gas law using kinetic molecular arguments by neglecting all intermolecular forces in the gas. In this chapter we apply similar kinetic molecular arguments to solids and liquids, but we cannot neglect the intermolecular forces. Consequently, the discussion of solids and liquids is more qualitative than that for gases.

10.1 Bulk Properties of Gases, Liquids, and Solids: Molecular Interpretation

Each of the following measurements provides clear distinctions among gases, liquids, and solids and also probes the strength of intermolecular forces, albeit indirectly. Each demonstrates that in gases at low densities, molecules are on average far apart and interact only weakly; in condensed phases, molecules are closely packed together and interact quite strongly. These general conclusions apply almost universally to substances consisting of small, nearly rigid molecules such as N_2, CO_2, CH_4, and acetic acid $C_2H_4O_2$. In contrast, many biological materials and synthetic polymers contain complex chainlike molecules that can become strongly entangled. Clear-cut classification of these materials as solids or liquids becomes difficult.

Interpreting bulk properties qualitatively on the basis of microscopic properties requires only consideration of the long-range attractive forces and short-range repulsive forces between molecules; it is not necessary to take into account the details of molecular shapes. We have already shown one kind of potential that describes these intermolecular forces, the Lennard–Jones 6–12 potential used in Section 9.7 to obtain corrections to the ideal gas law. In Section 10.2, we discuss a variety of intermolecular forces, most of which are derived from electrostatic (Coulomb) interactions, but which are expressed as a hierarchy of approximations to exact electrostatic calculations for these complex systems.

Molar Volume

One mole of a typical solid or liquid occupies a volume of 10 to 100 cm^3 at room conditions, but the **molar volume** of a gas under the same conditions is about 24,000 $cm^3\ mol^{-1}$. This large difference explains why solids and liquids are called the condensed states of matter. Because a mole of any substance contains Avogadro's number of molecules, the molar volume is inversely related to the **number density** (number of molecules per cubic centimeter) of the different phases. Liquids and solids have high number densities, and gases have very low number densities. On melting, most solids change volume by only 2% to 10%, showing that the solid and liquid states of a given substance are condensed, relative to the gaseous state, by roughly the same amount.

The similarity of the molar volumes of solid and liquid forms of the same substance suggests that the separation between neighboring molecules in the two states is approximately the same. Density measurements (see Section 2.1) show that the intermolecular contacts, the distances between the nuclei of atoms at the far edge of one molecule and the near edge of a neighbor, usually range from 3×10^{-10} m to 5×10^{-10} m in solids and liquids. At these distances, longer range

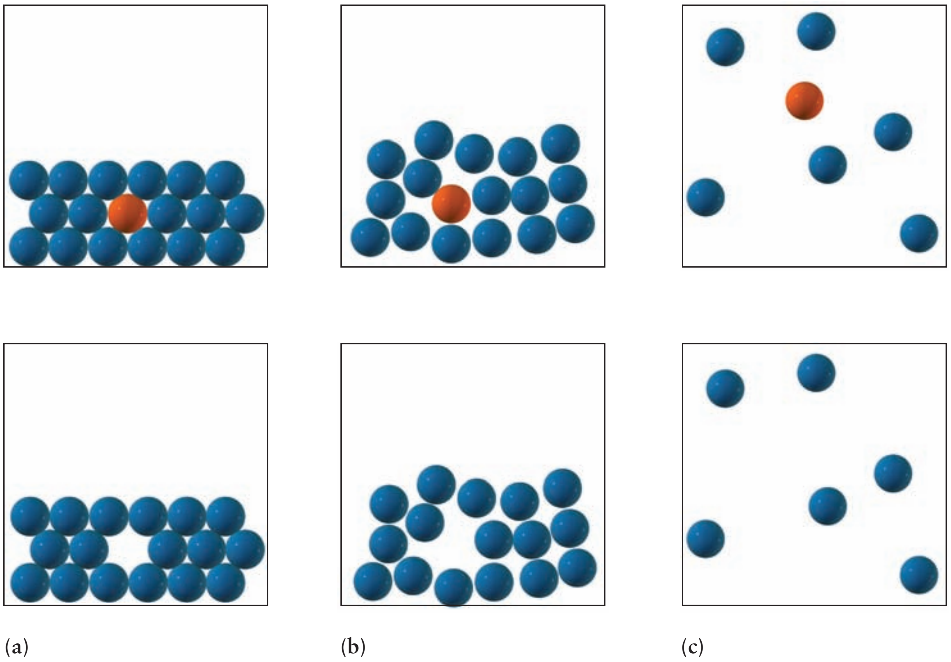


FIGURE 10.1 Intermolecular forces create structure in liquids and solids. If a single atom is removed from a snapshot of the atomic arrangement in a solid (a), it is easy to figure out exactly where to put it back in. For a liquid (b), the choices are limited. If a single atom is removed from a gas (c), no clue remains to tell where it came from.

attractive forces and shorter range repulsive forces just balance one another, resulting in a minimum in the potential energy (see Section 9.7). Although these intermolecular separations are significantly greater than chemical bond lengths (which range from $0.5–2.5 \times 10^{-10}$ m), they are much shorter than the intermolecular separations in gases, which average about 30×10^{-10} m under room conditions. The distinction is shown schematically in Figure 10.1.

Compressibility

The **compressibility** of a substance is defined as the fractional decrease in volume per unit increase in pressure. The compressibility is usually denoted by the Greek letter kappa, κ, and is defined operationally by its method of measurement: $\kappa = -(1/V)(\Delta V/\Delta P)$. A sample with volume V is subjected to a pressure increase, ΔP, and the resulting change in volume, ΔV, is measured. The result is divided by V; thus, the tabulated value depends only on the substance being measured and not on the geometry of the sample. Consequently, the unit of κ is P^{-1}. The minus sign is included in the definition to make κ positive because ΔV is negative. The measurements are always performed at fixed temperature to eliminate any thermal effects on the volume (see later). Consequently, κ is called the *isothermal compressibility,* and the temperature of measurement is quoted together with the tabulated values. Both solids and liquids are nearly incompressible, but gases are very compressible. According to Boyle's law, doubling the pressure exerted on an ideal gas from 1 to 2 atm reduces its volume by half (at constant temperature). The corresponding compressibility is 2 atm^{-1} or 20 MPa^{-1}. Doubling the pressure exerted on water or steel scarcely changes the volume at all; typical compressibilities for these materials are of the order 10^{-5} to 10^{-6} atm^{-1} (Table 10.1). Increasing the pressure on a liquid or solid by a factor of 2 changes its volume by 1% or less. The high compressibility of gases and the low compressibilities of solids and liquids suggest that in the gas phase there is substantial space between the molecules, but in the condensed states the particles of a substance are in contact or nearly in contact.

The much greater separation between molecules in the gas phase than in the condensed phases dramatically influences the effect of intermolecular forces. The repulsive force, although very strong, is very short-ranged and becomes

TABLE 10.1 Isothermal Compressibility[†] and Thermal Expansion Coefficients

Compound	$\kappa/(10^{-6}\ \text{atm}^{-1})$	$\alpha/(10^{-4}\ K^{-1})$
Liquids		
Benzene	92.1	12.4
Ethanol	76.8	11.2
Mercury	38.7	1.82
Water	49.7	2.1
Solids		
Copper	0.735	0.501
Diamond	0.187	0.030
Iron	0.597	0.354
Lead	2.21	0.861

[†] Values at 20°C.

significant only when molecules are very close together. So, gases require only modest forces to compress them significantly, because the molecules can be pushed much closer together before experiencing repulsive forces. Liquids and solids require much greater forces to oppose the strongly repulsive forces already operating because the molecules are in contact (see Section 9.7).

Thermal Expansion

The **coefficient of thermal expansion** α is defined as the fractional increase in the volume of a substance per degree increase in temperature. Like the compressibility, it is defined operationally by its method of measurement: $\alpha = (1/V)(\Delta V/\Delta T)$. The measurements are performed at constant pressure; thus, α is called the *isobaric coefficient of thermal expansion*, and the pressure at which the measurements were taken is quoted together with tabulated values. Charles's law shows that this coefficient is the same for all gases and takes the value $1/273.15(°\text{C})^{-1}$ at 0°C. Increasing the temperature by 1°C thus causes a gas to expand by 1/273.15, or 0.366% of its original volume at 0°C, as long as the pressure is constant. The thermal expansion coefficients of liquids and solids are much smaller. Heating water from 20°C to 21°C increases its volume by only 0.0212%, and the volume of mercury goes up by only 0.0177% over the same temperature interval. The coefficients of thermal expansion of solids are mostly less than 0.02% per degree Celsius (see Table 10.1).

The difference in thermal expansion between condensed states and gases is explained by strong intermolecular forces (deep intermolecular potential wells) acting over short distances in the condensed states, but not in the gaseous state. Because of the much greater intermolecular separations, these forces are much weaker in gases. An increase in volume in a solid or liquid requires that attractive forces between each molecule and its neighbors be partially overcome. Because the intermolecular distances in a solid or liquid fall in the range where intermolecular attractive forces are strongest, relatively small expansion occurs when the temperature is increased. By contrast, molecules in a gas are so far apart that attractive forces are essentially negligible; the same temperature increase produces much greater expansion in a gas than in condensed phases.

Fluidity and Rigidity

The most characteristic property of gases and liquids is their **fluidity,** which contrasts with the **rigidity** of solids. Liquids possess definite volumes but keep no definite shapes of their own; they flow easily under stress (externally applied mechanical force). The resistance of a material to macroscopic flow is measured by its **shear viscosity.** On the microscopic level, shear viscosity arises from the resistance of one thin layer of molecules "dragged across" another thin layer. The shear viscosities of most liquids are about 16 orders of magnitude smaller than those of most solids, and those of gases are smaller yet. A *rigid* material retains its shape under stress; it manifests structural strength by resisting flow when stress is applied. The properties of **hardness** (resistance to indentation) and **elasticity** (capacity to recover shape when a deforming stress is removed) are closely related to rigidity, or high shear viscosity. Solids possess these properties in good measure; gases and liquids do not.

Diffusion

When two different substances are placed in contact—for example, a drop of red ink into a beaker of water—they start to mix. Molecules of one type migrate, or **diffuse,** into regions initially occupied only by the other type. Molecules dispersed in gases at room conditions diffuse at rates on the order of centimeters per second. If you have ever passed by a perfume counter, this rate should not surprise you. Molecules in liquids and solids diffuse far more slowly. The **diffusion constant** of a substance measures the rate of diffusive mixing. At room temperature and pressure, diffusion constants for the diffusion of liquids into liquids are about four orders of magnitude smaller than those for gases into gases; diffusion constants of solids into solids are many orders of magnitude smaller yet. Diffusion in solids is really quite slow. Values of the diffusion constant for selected materials are shown in Table 10.2.

Figure 10.1 shows a "snapshot" of a liquid and a solid, fixing the positions of the atoms at a particular instant in time. The paths followed by the molecules in these two states can also be examined over a short time interval (Fig. 10.2). In liquids, molecules are free to travel through the sample, changing neighbors constantly in the course of their diffusive motion. In a solid, the molecules constantly vibrate about their equilibrium positions, but remain quite close to those positions. The low shear viscosity of a liquid implies that its molecules can quickly change neighbors, finding new interactions as the liquid flows in response to an external stress. The rigidity of solids suggests, in contrast, a durable arrangement of neighbors about any given molecule. The durable arrangement of molecules in a solid, as opposed to the freedom of molecules to diffuse in a liquid at comparable packing density, is the critical difference between the solid and liquid states.

TABLE 10.2 Diffusion Constants

Diffusing Species	Host Material	Diffusion Constant (m^2/s^{-1})	Temperature (K)
Ar	Ar	2.3×10^{-6}	100
Ar	Ar	1.86×10^{-5}	300
N_2	N_2	2.05×10^{-5}	300
O_2	O_2	1.8×10^{-5}	273
CH_4	CH_4	2.06×10^{-5}	273
HCl	HCl	1.24×10^{-5}	295
Cu	Cu	4.2×10^{-19}	500
Al	Al	4.2×10^{-14}	500
Cu	Al	4.1×10^{-14}	500
Cu	Ni	1.3×10^{-22}	500
Fe	Fe	3.0×10^{-21}	500
Fe	Fe	1.8×10^{-15}	900
C	Fe	1.7×10^{-10}	900

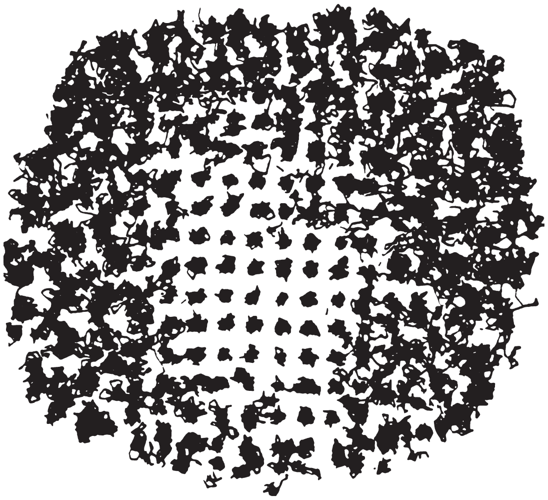


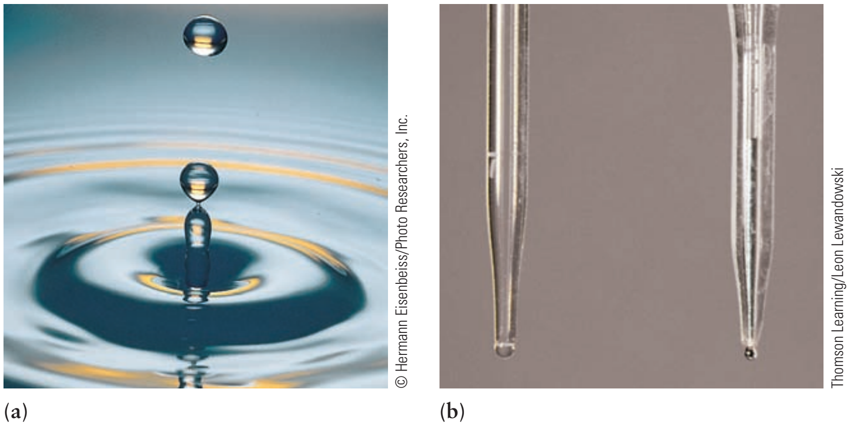
FIGURE 10.2 In this computer-simulated picture of the motions of atoms in a tiny melting crystal, the atoms at the center (in the solid) move erratically about particular sites. The atoms at the surface (in the liquid) move over much greater distances.

Short-range attractive intermolecular forces in liquids lead to well-defined local structures that persist for short periods. Individual molecules experience interactions with neighbors that lead, at any instant, to a local environment closely resembling that in a solid, but they quickly move on. Their trajectories consist of "rattling" motions in a temporary cage formed by neighbors and superimposed on erratic displacements over larger distances. In this respect, a liquid is intermediate between a gas and a solid. A gas (see Fig. 9.22) provides no temporary cages, so each molecule of a gas travels a longer distance before colliding with a second molecule. Consequently, the diffusion constant of a gas is larger than that of a liquid. In a solid, the cages are nearly permanent, thus diffusion is slow. Melting occurs as thermal energy increases the amplitude of vibration of the molecules around their equilibrium positions in a solid to such a degree that they are free to make major excursions. For these same reasons, liquids can dissolve substances much more rapidly than do solids. Individual molecules of a liquid quickly wander into contact with molecules of an added substance, and new attractions between the unlike molecules have an early chance to replace those existing originally in the pure liquid.

Liquids and gases may also mix through **convection,** as well as by diffusion. In convection, the net flow of a whole region of fluid with respect to another region leads to mixing at far greater rates than occurs through simple diffusion. Convection is the primary mechanism by which mixing occurs in the oceans and in the atmosphere. Convection is not observed in solids.

Surface Tension

Boundaries between phases have special importance in chemistry and biology. Each type of boundary has its own unique characteristics. The surface of water (or any liquid) in contact with air (or any gas) resists attempts to increase its area (Fig. 10.3a). This **surface tension** causes the surface to behave like a weak, elastic skin. Effects of surface tension are particularly apparent under zero gravity, where liquids float around as spherical drops because spheres contain the largest volume for the smallest surface area of any geometric shape. If two small drops encounter each other, they tend to coalesce into a larger drop because one large drop has a smaller surface area than two small drops. The surface tension of water is larger than that of most other liquids at room temperature, but it is about six times smaller than that for the liquid metal mercury, which has one of the highest values known for any liquid at room temperature and pressure (see Fig. 10.3b).



(a) (b)

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FIGURE 10.3 (a) Surface tension causes the spherical shape of the water droplet in this photograph, which was taken an instant after a drop of water hit the surface of a pool and bounced up, pulling with it a column of water. (b) The mercury drop at the dropper tip on the right is a nearly perfect sphere, whereas the water drop on the left sags slightly. This is evidence of the higher surface tension of the mercury, the drops of which resist the deforming pull of gravity more effectively than those of water.

Surface tension results from the intermolecular attractions among the molecules in a liquid (Fig. 10.4). Increasing the surface area of a liquid requires redistributing some of the molecules that were originally buried in the interior to positions at the enlarged boundaries. Molecules at the edges have no neighbors on one side and experience attractions only from molecules in the bulk of the liquid. Their potential energy is greater than it would be if they were in the interior. Thus, energy is required to increase the surface area of a liquid. Liquids such as water and mercury with high values of surface tension have particularly strong intermolecular attractions, as confirmed by measurement of other properties.

10.2 Intermolecular Forces: Origins in Molecular Structure

To provide a more quantitative explanation of the magnitudes of the properties of different materials, we must consider several types of intermolecular forces in greater detail than we gave to the Lennard–Jones model potential in Chapter 9. The Lennard–Jones potential describes net repulsive and attractive forces between molecules, but it does not show the origins of these forces. We discuss other intermolecular forces in the following paragraphs and show how they arise from molecular structure. Intermolecular forces are distinguished from *intramolecular* forces, which lead to the covalent chemical bonds discussed in Chapters 3 and 6. Intramolecular forces between atoms in the covalent bond establish and maintain

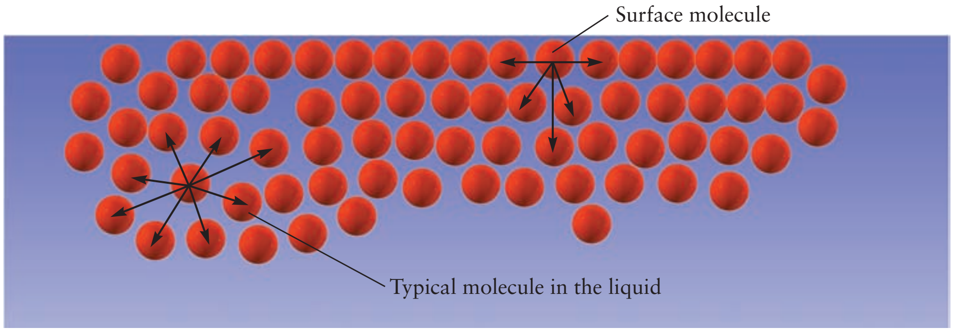


FIGURE 10.4 The intermolecular attractions acting on a molecule at the surface of a liquid pull it downward and to the sides but not upward. In the interior, a molecule is pulled more or less equally in all directions.

the structure of discrete molecules: They are strong, directional, and comparatively short ranged. Intermolecular forces differ from intramolecular forces in several important ways:

1. Intermolecular forces are generally weaker than covalent chemical bonds. For example, it takes 239 kJ to break 1 mol of Cl—Cl covalent bonds, but only 1.2 kJ to overcome 1 mol of Ar—Ar attractions.
2. Intermolecular forces are much less directional than covalent chemical bonds.
3. Intermolecular forces operate at longer range than covalent chemical bonds.

All intermolecular and intramolecular forces arise because matter is composed of electrically charged particles whose interactions with one another are all described by Coulomb's Law. Although we could, in principle, calculate the force by summing all of the attractive and repulsive interactions between the charged particles, it is useful to distinguish different classes of forces based on their strength, directionality, and range. The physical and chemical properties of liquids and solids can often be interpreted or even predicted by considering the types of intermolecular force that dominate in their internal structures.

Ion–Ion Forces

The units of organization in ionic solids and liquids are electrically charged entities, sometimes monatomic ions such as Na^+, Cl^-, and Ca^{2+}, and sometimes polyatomic ions such as NH_4^+ and SO_4^{2-}. The dominant interaction among these ions is the Coulomb force of electrostatic attraction or repulsion, which leads to the Coulomb potential described in Section 3.2. Ions of like charge repel one another, and ions of unlike charge attract one another. These **ion–ion forces** can be as strong as those in the covalent bond, and they are long ranged. The potential energy is proportional to R^{-1} and decreases much less rapidly with distance than do the strengths of other types of interactions. Ion–ion forces are not directional; each ion interacts equally strongly with neighboring ions on all sides. Ion–ion forces lead to the formation of ionic bonds through the Coulomb stabilization energy (see Section 3.6).

Dipole–Dipole Forces

The dominant force between polar molecules is the **dipole–dipole force.** This is a second example of electrostatic forces that arise from interactions between fixed charges, in this case the magnitudes of the permanent dipole moments of polar molecules. As shown in Figure 10.5, these forces also depend on the orientations of the two molecules and can be either attractive or repulsive or zero. Random motions of polar molecules in gases and liquids lead to a variety of energetically favorable temporary dipole–dipole orientations. The potential energy between dipoles separated by the distance R falls off as R^{-3}. This potential decreases much more rapidly with separation than does the Coulomb potential between ions. Separating a pair of ions by a factor of 10 reduces the Coulomb potential energy by only a factor of 10, whereas separating a pair of dipoles by a factor of 10 reduces the potential energy by a factor of 1000. In liquids, thermal energy can overcome dipole–dipole attractions and disrupt favorable orientations; dipole–dipole interactions are too weak to hold molecules in a liquid together in a nearly rigid arrangement. Nonetheless, they are sufficiently strong to influence many physical properties, including boiling points, melting points, and molecular orientations in solids.

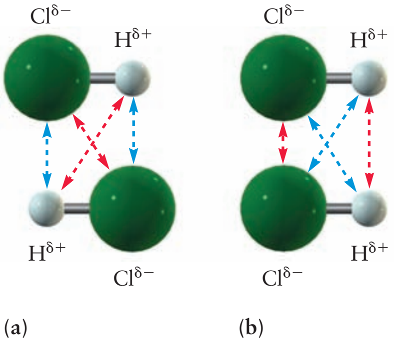


FIGURE 10.5 A molecule of HCl can be represented as having a small net negative charge on the Cl end, balanced by a small net positive charge on the H end. The forces between two HCl molecules depend on their orientations. (a) The oppositely charged ends (blue arrows) are closer than the ends with the same charge (red arrows). This gives a net attractive force. (b) Here, the opposite is true, and the net force is repulsive.

Ion–Dipole Forces

A third example of electrostatic forces occurs when a polar molecule is near an ion. The interaction between a polar solvent molecule, such as water, and a

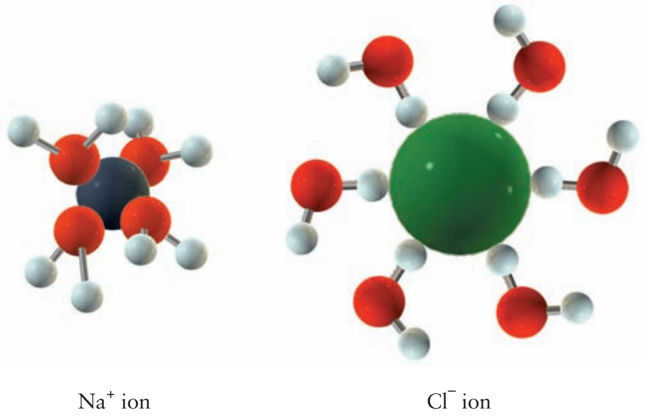


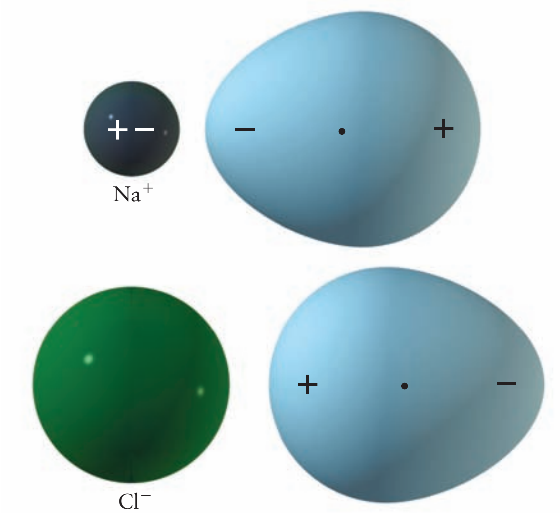
FIGURE 10.6 Solvation of ions in liquid water. The water molecules have dipole moments; thus, the oxygen (O) atoms bear small, negative charges, whereas the hydrogen (H) atoms bear small, positive charges. (a) Positive ions are attracted to neighboring water molecules in aqueous solution by ion–dipole forces. (b) Negative ions form hydrogen bonds with water, with a nearly linear bond from O to H to the anion.

dissolved ion is the most common case of ion–dipole interaction. Figure 10.6 shows dissolved Na^+ and Cl^- ions interacting with water dipoles. Positive ions are attracted by the negative end of the dipole and repelled by the positive end; thus, the ion is surrounded by a shell of water molecules whose oxygen (O) atoms are near the cation and whose hydrogen (H) atoms point outward into the solution. For many years it was believed that the opposite would be true for negative ions, that they would be surrounded by a shell of water dipoles whose H atoms were both near the anion. Since about 1980, neutron diffraction has been used to determine the distances between atoms in ionic aqueous solutions. A series of such studies has shown that the halide anion interacts with only one of the H atoms, and the atoms O—H—Cl lie nearly in a straight line. The other H atom points in a direction determined by the geometry of the water molecule. The solvation of the anion is not governed by ion–dipole forces. Rather, the O—H—Cl interaction is an example of the *hydrogen bond,* a special intermolecular force that occurs only in liquids. The hydrogen bond is discussed in the next section, and the solvation of ions is discussed more thoroughly in Chapter 11.

Induced Dipole Forces

The electrons in a nonpolar molecule or atom are distributed symmetrically, but the distribution can be distorted by an approaching electrical charge. An argon (Ar) atom has no dipole moment, but an approaching Na^+, with its positive charge, attracts the electrons on the side near it more strongly than those on the far side. By tugging on the nearby electrons harder, Na^+ induces a temporary dipole moment in the Ar atom (Fig. 10.7). The electron distribution of the nonpolar molecule is said to be *polarizable,* and the magnitude of the dipole moment induced measures the **polarizability** of the molecule. As long as the induced dipole is present, the interaction between molecules is similar to the ion–dipole case just described. **Induced dipole forces** also can be caused by a negative ion or by another dipole. These so-called induction forces differ from the electrostatic forces between permanent fixed charges such as ions or dipoles. Rather, they arise from interactions between the permanent charges or moments on one molecule and the induced moments, or the polarizability, of another molecule. These interactions are weak and are effective only at short range. The induced dipole moment closely tracks the motion of the charge or dipole moment of the inducing molecule. The induced dipole is dynamically correlated with the motion of the inducing molecule. A good way to study induced dipole forces quantitatively is to collide a beam of Na^+ ions and a beam of Ar atoms in vacuum, measure the energy and direction of their deflections, and deduce the correct potential function to explain these deflections.

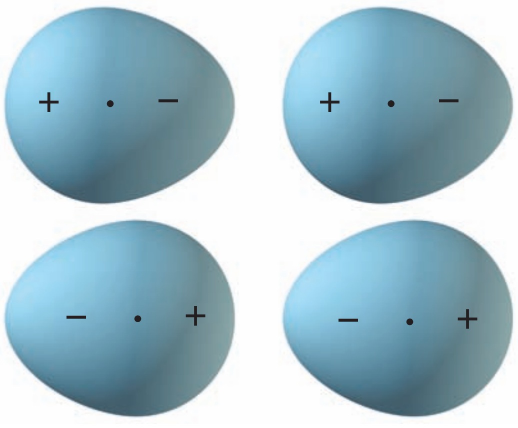
FIGURE 10.7 As an ion approaches an atom or molecule, its electrostatic field distorts the distribution of the outer electrons. The effect of this distortion is to create a dipole moment that exerts an attractive force back on the ion.



Induced Dipole–Induced Dipole Forces: London Dispersion Forces

Helium (He) atoms, like the atoms of the other noble gases, are electrically neutral and nonpolar, so none of the forces discussed so far explains the observed fact that there are attractions between He atoms. We know such attractions must exist, because helium becomes a liquid at 4.2 K and 1 atm. Attractions between neutral, nonpolar atoms or molecules arise from the **London dispersion forces** (often called van der Waals forces) that exist between all atoms and molecules. Dispersion forces are, in effect, a mutual interaction between the polarizable charge distributions on two separate molecules, and they are always attractive. Although the electron probability distribution around the molecule is described by the square of the wave function, dynamic motions of charge around the molecule can lead to an instantaneous, temporary dipole moment. Such a temporary dipole on one molecule will induce a temporary dipole in the other molecule. These transient, fluctuating dipoles attract one another in much the same way as do permanent dipoles. Figure 10.8 provides a simple view of the source of this interaction. The polarizability increases with the number of electrons in the atom or molecule. Heavier atoms or molecules interact more strongly by dispersion forces than do lighter ones because their electrons are located in shells farther from the nucleus. These electrons are less strongly bound than those of the lighter elements, because they are shielded from the full attraction of the nucleus by intervening

FIGURE 10.8 A fluctuation of the electron distribution on one atom induces a corresponding temporary dipole moment on a neighboring atom. The two dipole moments interact to give a net attractive force, called a "dispersion force."



electrons (see Sections 3.2 and 5.2). Consequently, they are more easily distorted by external fields of neighboring dipoles. Dispersion forces are always attractive and fall off as R^{-6}. These interactions are short ranged, much more so than dipole–dipole forces. Dispersion forces provide the attractive term in the Lennard–Jones potential (see description in Section 9.7).

Repulsive Forces

As atoms or molecules approach each other closely, **repulsive forces** come into play and can overcome the attractive forces considered so far. The source of these forces is the strong repulsion between the core (nonvalence) electron clouds when neighboring atoms are forced close to each other. This contribution is negligible until the distance between centers becomes small, at which point the repulsive energy increases rapidly as distance is reduced further. Two mathematical models are used to describe repulsive forces, although neither has a simple physical foundation to guide the choice of the parameters involved. The exponential form $Ae^{-R/\rho}$ is successful when A and ρ are chosen to fit experimental data such as compressibility measurements. The inverse power form R^{-n}, where n is quite large, is also successful. The choice $n = 12$ is widely used because, when combined with the $n = 6$ choice to describe attractive forces, the resulting Lennard–Jones potential reproduces the trends in experimental data over significant ranges. Regardless of mathematical form, this steep, repulsive interaction at extremely small distances justifies modeling atoms as hard, nearly incompressible spheres with characteristic dimensions called the **van der Waals radii.** This label honors the early contributions of Johannes van der Waals to the study of nonbonded interactions between molecules and their influence on the properties of materials. The minimum distance between molecules in a condensed phase is determined by the sum of the van der Waals radii of their atoms. Space-filling models and drawings are usually designed to approximate the van der Waals surface of molecules, which represents the distance of closest approach by neighboring molecules. Van der Waals radii for atoms are typically a few angstroms (Å).

EXAMPLE 10.1

State which attractive intermolecular forces are likely dominant in the following substances:

(a) $F_2(s)$

(b) $HBr(\ell)$

(c) $NH_4Cl(s)$

SOLUTION

(a) Molecules of F_2 are nonpolar, thus the predominant attractive forces between molecules in $F_2(s)$ come from dispersion.

(b) The HBr molecule has a permanent dipole moment. The predominant forces between molecules are dipole–dipole. Dispersion forces will also contribute to associations, especially because Br is a rather heavy atom.

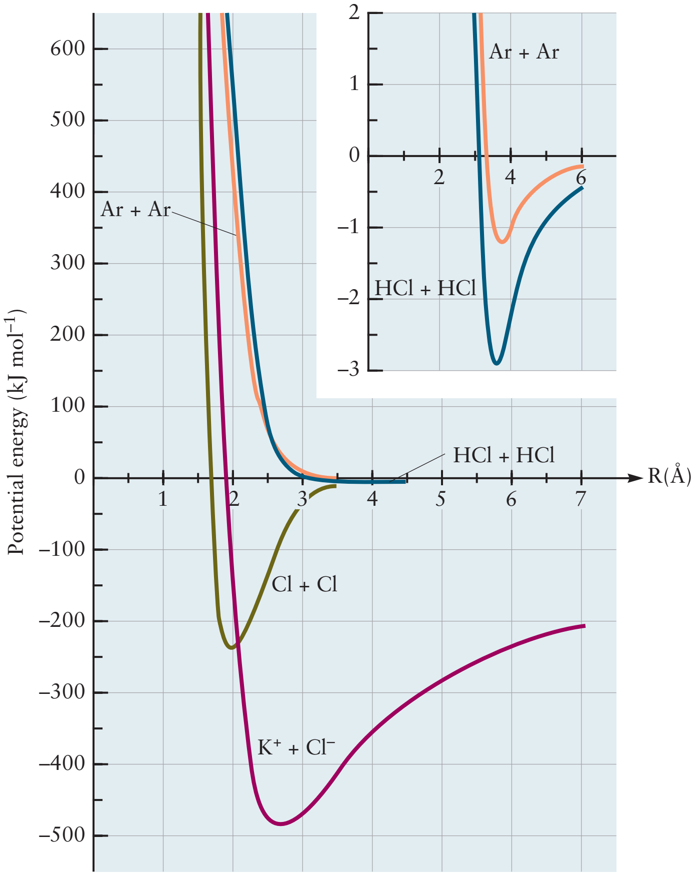
(c) The ammonium ions are attracted to the chloride ions primarily by ion–ion forces.

Related Problems: 15, 16, 17, 18, 19, 20

Comparison of Potential Energy Curves

The relative strengths and effective ranges of several intermolecular forces are illustrated in Figure 10.9, which shows how the potential energy depends on the

FIGURE 10.9 The potential energy of a pair of atoms, ions, or molecules depends on the distance between the members of the pair. Here, the potential energy at large separations (to the right side of the graph) is arbitrarily set to zero by convention (see Section 3.2). As pairs of particles approach each other, the potential energy becomes negative because attractive forces come into effect. The lowest point in each curve occurs at the distance where attractive and repulsive forces exactly balance. The relative potential energy values at these minima measure the relative strength of the attractive forces in the various cases illustrated. Note the shallow potential energy minimum for hydrogen chloride (HCl) and argon (Ar). (inset) The inset shows these same two curves with the vertical scale expanded by a factor of 100. (The HCl–HCl curve was computed for the relative orientations of Fig. 10.5a.)



intermolecular separation (center-to-center distance) for several pairs of ions, atoms, and molecules. The potentials illustrated here include Coulomb (R^{-1}), dipole–dipole (R^{-3}), dispersion (R^{-6}), and repulsive (R^{-12}) potentials. The species shown in Figure 10.9 were chosen so that the interacting atoms, ions, or molecules have the same number of electrons (Ar, Cl^-, K^+, HCl). For comparison, the covalent bond (*intra*molecular force) for Cl_2 is also shown. The ion–ion interaction of K^+ with Cl^- is the strongest (stronger even than the covalent interaction in Cl_2), followed by the interaction between two HCl molecules (dipole–dipole and dispersion) and the Ar–Ar interaction (dispersion only). The key points illustrated here (and detailed in the caption for Fig. 10.9) are the dramatically different depths of the wells (several orders of magnitude), as well as the distinctly different distances at which the minima occur.

The Shapes of Molecules and Electrostatic Forces

The potential energy diagrams in Figure 10.9 depend only on the distance between the two species. Interactions between complex molecules also depend strongly on their relative orientations, so we need a three-dimensional generalization of the potential energy diagram to describe these interactions more fully. This need could be met by constructing a potential energy *surface* where the interaction energy is plotted as a function of all three spatial coordinates that locate the center of one molecule relative to the center of the other. Because quantitative calculations of intermolecular forces are not yet available from quantum mechanics, we use approximate representations to describe the influence of shape and orientation as two molecules approach one another. One such approximate representation is the **electrostatic potential energy map,** which shows the shape and size of the molecule, as well as the sign and magnitude of the electrostatic potential at the "surface" of the molecule.

The electrostatic potential energy map for a molecule combines information from two different sources into one representation. The size and shape of the molecule come from the spatial distribution of the electron density represented as an isosurface. The electrostatic potential energy that a positive test charge would experience is indicated at each point on that isosurface. Let's construct each of these pieces in turn.

Isosurfaces of electron density are obtained from the probability density isosurfaces for molecules described in Chapter 6. These are surfaces in three-dimensional space that include all the points at which ψ^2 has a particular value. The value of electron density chosen to define the isosurface is selected by some definite, though arbitrary, criterion. There is broad acceptance of a standard density of 0.002 $e/(a_0)^3$, where a_0 is the Bohr radius. This value is thought to best represent the "sizes" and shapes of molecules because it corresponds to the van der Waals atomic radii discussed earlier in the context of repulsive forces. These are the same dimensions depicted in space-filling models of molecules.

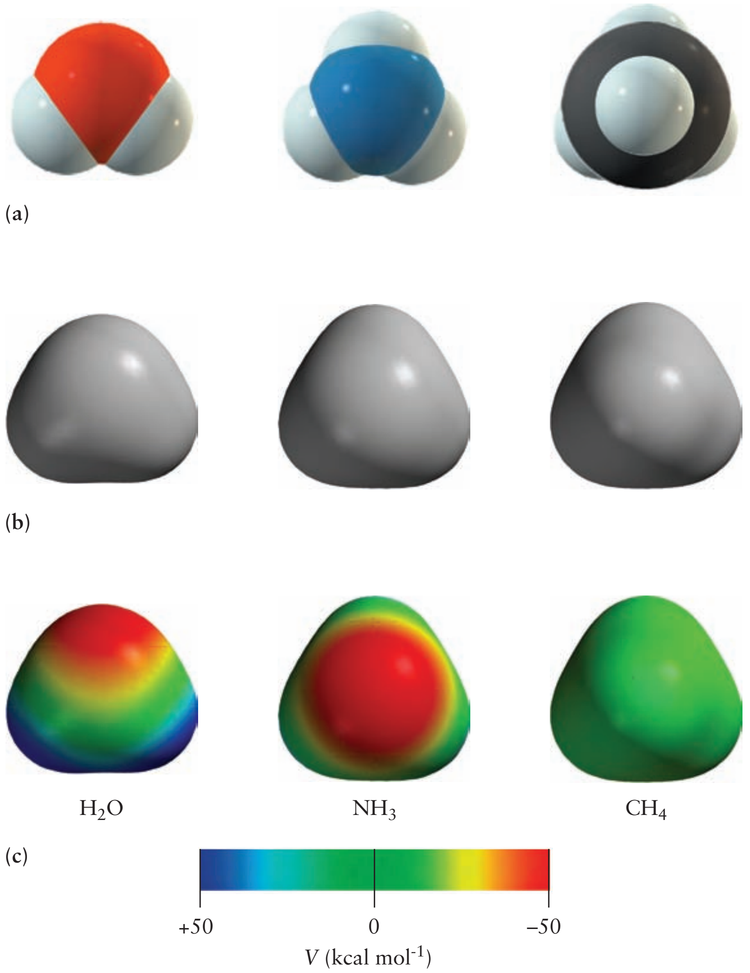


FIGURE 10.10 (a) Space-filling models, (b) 0.002 $e/(a_0)^3$ electron density isosurfaces, and (c) electrostatic potential energy surfaces for water, ammonia, and methane.

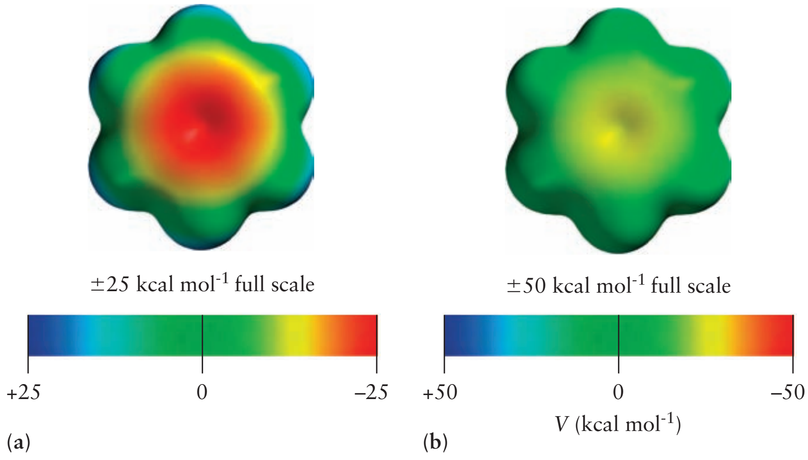


FIGURE 10.11 Electrostatic potential energy surfaces for benzene plotted at ±25 (a) and ±50 kcal mol^{-1} full scale (b), respectively.

Figures 10.10a and b show, respectively, space-filling models and electron density isosurfaces plotted at 0.002 $e/(a_0)^3$ for water, ammonia, and methane. The electron densities plotted here include all of the electrons in the molecule. They are calculated using state-of-the-art *ab initio* quantum chemical methods (see discussion in Chapter 6).

To understand how a value of the electrostatic potential energy can be associated with each point on the electron density isosurface, we imagine a thought experiment in which a positive unit test charge crawls like an insect over this isosurface, interacting with all of the electrons and the nuclei of the molecule as it visits every position on the isosurface. The magnitude of the test charge must be extremely small to avoid distorting and polarizing the electron density of the molecule (see Figure 10.7). The test particle is attracted to the molecule at those points where it experiences negative electrostatic potential energy, and it is repelled away from the molecule at points where it experiences positive electrostatic potential energy. It is convenient to summarize these explorations by assigning color to each location on the isosurface on the basis of the sign and magnitude of the electrostatic potential energy experienced by the test charge. The conventional choice for the color map is the visible spectrum, in which the most negative potential is represented by red and the most positive potential is represented by blue. The colors assigned to each point on the electron density isosurface vary continuously between these extremes on the basis of the sign and magnitude of the electrostatic potential energy. The potential energy values near zero are represented by green.

The actual values of electrostatic potential energy are obtained through computer calculations as follows. After the electron density isosurface has been calculated by quantum mechanics, a small positive test charge is moved around the molecule at locations corresponding to points on the isosurface. At each location the electrostatic potential energy is calculated using Coulomb's law to describe the interaction of the test charge with each nucleus and each electron in the molecule. At each location, the value of the electrostatic potential energy represents the balance between attraction of the test charge by electrons and repulsion by the nuclei in the molecule. The value obtained at each location of the test particle is then mapped onto the corresponding point on the electron density isosurface for the molecule by assigning color according to the color map. The electrostatic potential energy maps calculated for the molecules shown in Figures 10.10a and b are shown in Figure 10.10c.

The numerical value of the most negative potential value (assigned to red) and the most positive value (assigned to blue) can be adjusted to emphasize features of interest in a particular study. Figure 10.11 illustrates this fact by showing the electrostatic potential energy maps for benzene plotted for the ranges ±25 and ±50 kcal mol^{-1}. In the second case, where red is assigned to -50 kcal mol^{-1}, the values for the region in the center of the benzene ring appear in the yellow-green range and are difficult to distinguish from the surrounding regions. Maps for different compounds plotted using the same energy range can be compared immediately, and trends in the behavior of these molecules toward approaching charged particles will be readily apparent.

The electrostatic potential energy map for a given molecule, called the "target" molecule, shows the spatial shape of the electrostatic field around the molecule, and so it can be used to predict how the target molecule influences the motion of charged particles as they approach it. The images show at a glance which portions of the molecule are most likely to attract or repel a proton (see Figure 10.10c). To an approaching proton, those regions colored red act as if they were three-dimensional attractive wells (valleys), whereas those colored blue act as if they were three-dimensional repulsive walls (mountains). Positive ions will be attracted to the oxygen end of the water molecule and to the nitrogen end of the ammonia molecule; the opposite is true for negative ions. The interaction of a positive or a negative ion with methane is weak and shows no pronounced directionality. Comparing Figure 10.10c with Figure 10.11b shows that a positive ion experiences greater attraction to the oxygen end of a water molecule and to the nitrogen end of an ammonia molecule than to the center of a benzene molecule.

Electrostatic potential energy maps can be used to identify reactive sites on molecules. Locations with large negative values of the electrostatic potential are relatively rich in electron density, and those with large positive values are relatively depleted in electron density. These maps are now widely used in organic chemistry to predict patterns of reactivity for electrophilic (electron-loving) and nucleophilic (proton-loving) molecules and to explain how the presence of different functional groups in the molecule can affect these patterns. These methods are effective aids in identifying sites for chemical reactivity in more complicated molecules, including those of biological interest. They are widely used in molecular modeling simulations of drug design.

10.3 Intermolecular Forces in Liquids

The same intermolecular forces that make gases deviate from ideal behavior (see Sections 9.7 and 10.2) are responsible for the existence of solids and liquids. At very high temperatures, these forces are negligible because the high kinetic energy of the molecules disrupts all possible attractions; all materials are gaseous at sufficiently high temperatures. At lower temperatures, where materials are in the liquid state, molecules are close together and the details of the intermolecular potential energy determine their properties. Section 10.2 describes the influence of molecular structure on the intermolecular potential energy. This section surveys the correlation between the properties of liquids and the structure of their constituent molecules. Special attention is given to the unusual properties of water.

Substances with strong attractive intermolecular forces tend to remain liquids at higher temperatures than those with weaker intermolecular forces; they have higher normal boiling points, T_b. Ionic liquids generally have the strongest attractions, because of the Coulomb interaction among charged ions, and thus have high boiling points. Molten NaCl, for example, boils at 1686 K under atmospheric

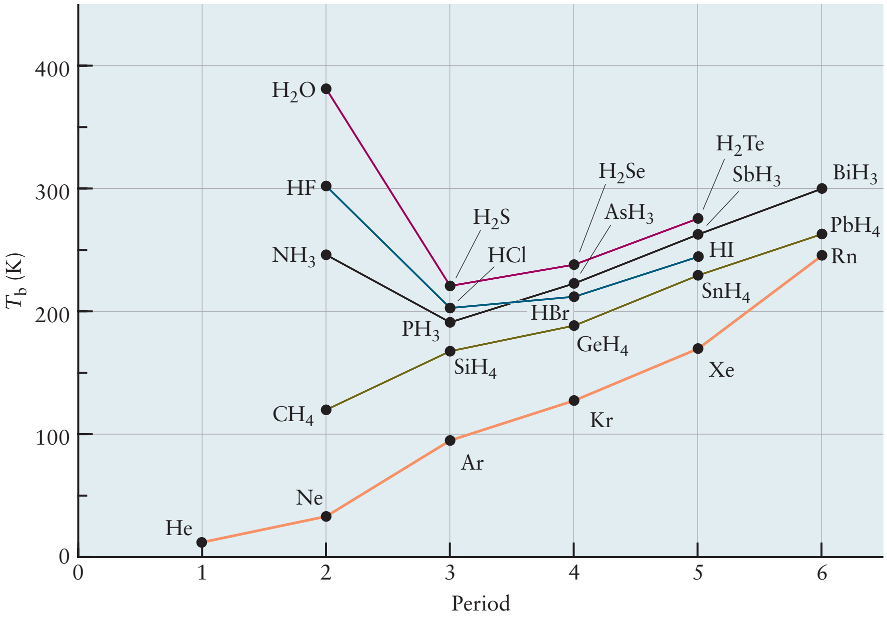


FIGURE 10.12 Trends in the boiling points of hydrides of some main-group elements and the noble gases.

pressure. At the opposite extreme, the normal boiling point of helium is only 4.2 K. Within a series of related compounds, those of higher molar mass tend to have higher normal boiling points. This trend arises from the increased polarizability of the heavier compounds, not from the increased mass per se. Progressing from helium to xenon, normal boiling points increase (Fig. 10.12), as do the strengths of the attractive dispersion forces among the noble gases. These forces, represented by the well depth ε in Table 9.4, arise from the polarizability of the atoms.

Between the noble-gas and ionic liquids falls a class of liquids called **polar liquids.** In liquid HCl, the molecules arrange themselves to the greatest extent possible with neighboring dipoles oriented to minimize the dipole–dipole potential energy. As described in Section 10.2, the dipole–dipole intermolecular forces in such polar liquids are weaker than the ion–ion Coulombic forces in ionic liquids but stronger than the dispersion forces in **nonpolar liquids** such as N_2. These three forces operate respectively between molecules in which the bonding is polar covalent, fully ionic, and fully covalent. As shown in Figure 10.12, HCl has a higher boiling point than argon (a nonpolar fluid of atoms with nearly the same molar mass) because of its polar nature. The magnitudes of the intermolecular forces in HCl and argon are compared explicitly in Figure 10.9.

Hydrogen Bonds

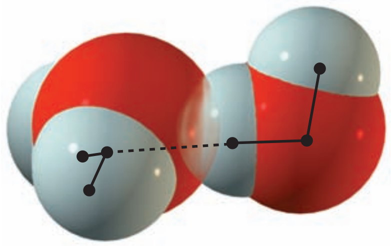


FIGURE 10.13 A single hydrogen bond between water molecules forms a dimer. This bond is far weaker than a covalent bond but still strong enough to resist dissociation at room temperature. The shared hydrogen (H) atom at the center approaches the neighboring oxygen (O) atom quite closely.

Figure 10.12 shows the normal boiling points of several series of hydrides, in which the boiling point increases with increasing molar mass in a series of related compounds. The dramatic deviations from these systematic trends shown by HF, NH_3, and especially H_2O indicate the strength and importance of the special type of bond that is common to these cases, a **hydrogen bond.** Such a bond forms when an H atom bonded to an O, N, or F atom (highly electronegative atoms) also interacts with the lone electron pair of another such atom nearby. Figure 10.13 shows the interaction of a pair of water molecules to form a dimer in the gas phase. The hydrogen bond that forms is weaker than an ordinary O—H covalent bond, but the interaction is significantly stronger than most other intermolecular interactions. Like most hydrogen bonds, that in water is nearly linear but asymmetric, with the H atom closer to and more strongly bound to one of the O atoms. It is indicated as O—H · · · O.

Water is a polar molecule, like HCl and H_2S. The water molecule is bent, as predicted by valence shell electron-pair repulsion theory and confirmed by experiment, and the orientation of its dipole moment (positive end toward the H atoms and negative end toward the O atom) has been related to its structure in Section 3.7. In the liquid, these molecules orient themselves in directions that minimize the potential energy between them; consequently, H atoms on one molecule are close to O atoms on neighboring molecules. The H atom in a bond such as O—H is surrounded by a relatively low density of negative charge because, unlike all other elements, it has no electrons other than valence electrons. As a result, it can approach close to the lone-pair electrons on a neighboring O atom, causing a strong electrostatic (Coulomb) interaction between the two. In addition, a small amount of covalent bonding arises from the sharing of electrons between the two O atoms and the intervening H atom. These effects combine to make the interaction unusually strong. For the same reason, hydrogen bonds form with anions in aqueous solution (see Fig. 10.6)

Special Properties of Water

Water makes up about 0.023% of the total mass of the earth. About 1.4×10^{21} kg of it is distributed above, on, and below the earth's surface. The volume of this vast amount of water is about 1.4 billion km^3. Most of the earth's water (97.7%) is contained in the oceans, with about 1.9% in the form of ice or snow and most of the remainder (a small fraction of the total) available as freshwater in lakes, rivers, underground sources, and atmospheric water vapor. A small but important fraction is bound to cations in certain minerals, such as clays and hydrated crystalline salts. More than 80% of the surface of the earth is covered with water—as ice and snow near the poles, as relatively pure water in lakes and rivers, and as a salt solution in the oceans.

The unusual properties of water, which come from its network of hydrogen bonds, have profound effects on life on earth. Figure 10.12 compares the boiling points of water and hydrides that lack hydrogen bonds. An extrapolation of the trends from the latter compounds would give a boiling point for "water without hydrogen bonds" near 150 K (−123°C). Life as we know it would not be possible under these circumstances.

If all possible hydrogen bonds form in a mole (N_A molecules) of pure water, then every oxygen atom is surrounded by four H atoms in a tetrahedral arrangement: its own two and two from neighboring molecules. This tetrahedral arrangement forms a three-dimensional network with a structure similar to that of diamond or SiO_2. The result is an array of interlocking six-membered rings of water molecules (Fig. 10.14) that manifests itself macroscopically in the characteristic sixfold symmetry of snowflakes.

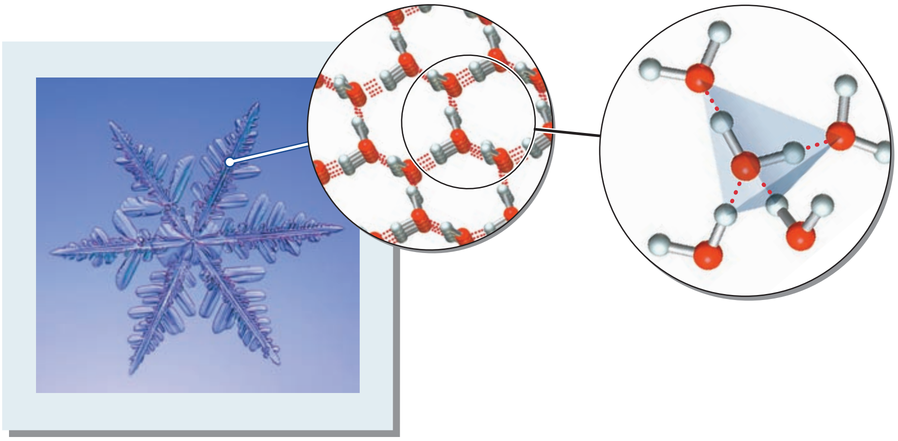


FIGURE 10.14 The structure of ice is quite open. Each water molecule has only four nearest neighbors with which it interacts by means of hydrogen bonds (red dashed lines).

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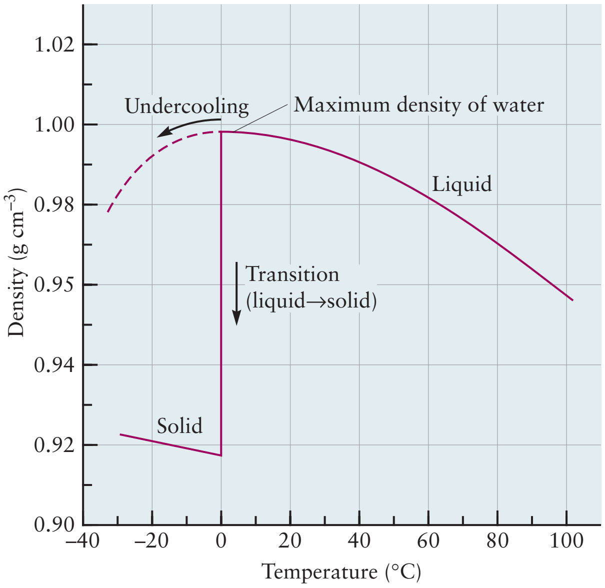


FIGURE 10.15 The density of water rises to a maximum as it is cooled to 3.98°C, then starts to decrease slowly. Undercooled water (water chilled below its freezing point but not yet converted to ice) continues the smooth decrease in density. When liquid water freezes, the density drops abruptly.

The density of water reaches its maximum at 4°C (Fig. 10.15), and it expands on freezing. This unusual behavior, which is seen in few other liquids, also is caused by hydrogen bonds. When ice melts, some of the hydrogen bonds that maintain the open structure shown in Figure 10.14 break and the structure partially collapses, producing a liquid with a smaller volume (higher density). The reverse process, a sudden expansion of water on freezing, can cause bursting of water pipes and freeze/thaw cracking of concrete. Such expansion also has many beneficial effects. If ice were denser than water, the winter ice that forms at the surface of a lake would sink to the bottom and the lake would freeze from the bottom up. Instead, the ice remains at the surface and the water near the bottom achieves a stable wintertime temperature near 4°C, which allows fish to survive.

EXAMPLE 10.2

Predict the order of increase in the normal boiling points of the following substances: F_2, HBr, NH_4Cl, and HF.

SOLUTION

As an ionic substance, NH_4Cl should have the highest boiling point of the four (measured value: 520°C). HF should have a higher boiling point than HBr, because its molecules form hydrogen bonds (see Fig. 10.10) that are stronger than the dipolar interactions in HBr (measured values: 20°C for HF, −67°C for HBr). Fluorine, F_2, is nonpolar and contains light atoms, and thus should have the lowest boiling point of the four substances (measured value: −188°C).

Related Problems: 23, 24

10.4 Phase Equilibrium

Liquids and solids, like gases, are **phases**—samples of matter that are uniform throughout in both chemical constitution and physical state. Two or more phases can coexist. Suppose a small quantity of liquid water is put in an evacuated flask, with the temperature held at 25°C by placing the system in a constant-temperature

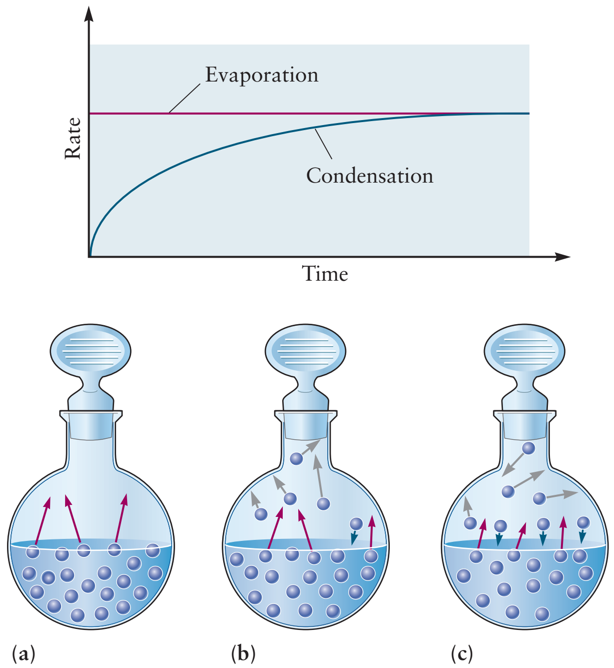


FIGURE 10.16 Approach to equilibrium in evaporation and condensation. Initially, the pressure above the liquid is very low, and many more molecules leave the liquid surface than return to it. As time passes, more molecules fill the gas phase until the equilibrium vapor pressure, P_{vap}, is approached; the rates of evaporation and condensation then become equal.

bath. A pressure gauge is used to monitor changes in the pressure of water vapor inside the flask. Immediately after the water enters the flask, the pressure of water vapor begins to rise from zero. It increases with time and gradually levels off at a value of 0.03126 atm, which is the **vapor pressure** of water at 25°C. The contents of the flask have reached **equilibrium,** a condition in which no further changes in macroscopic properties occur as long as the system remains isolated. This passage toward equilibrium is a spontaneous process, occurring in a closed system without any external influence. If some of the water vapor that has formed is removed, additional water evaporates from the liquid to reestablish the same vapor pressure, $P_{vap}(H_2O) = 0.03126$ atm.

What is happening on a microscopic scale to cause this spontaneous movement of the system toward equilibrium? According to the kinetic theory, the molecules of water in the liquid are in a constant state of thermal motion. Some of those near the surface are moving fast enough to escape the attractive forces holding them in the liquid; this process of **evaporation** causes the pressure of the water vapor to increase. As the number of molecules in the vapor phase increases, the reverse process begins to occur: Molecules in the vapor strike the surface of the liquid, and some are captured, leading to **condensation.** As the pressure of the gas increases, the rate of condensation increases until it balances the rate of evaporation from the surface (Fig. 10.16). Once this occurs, there is no further net flow of matter from one phase to the other; the system has reached **phase equilibrium,** characterized by a particular value of the water vapor pressure. Water molecules continue to evaporate from the surface of the liquid, but other water molecules return to the liquid from the vapor at an equal rate. A similar phase equilibrium is established between an ice cube and liquid water at the freezing point.

The vapor pressure of the water is independent of the size and shape of the container. If the experiment is duplicated in a larger flask, then a greater *amount* of water evaporates on the way to equilibrium, but the final pressure in the flask at 25°C is still 0.03126 atm as long as some liquid water is present. If the experiment is repeated at a temperature of 30.0°C, everything happens as just described, except that the pressure in the space above the water reaches 0.04187 atm. A higher temperature corresponds to a larger average kinetic energy for the water molecules. A new balance between the rates of evaporation and condensation is struck, but at a higher vapor pressure. The vapor pressure of water, and of all other substances, increases with rising temperature (Fig. 10.17; Table 10.3).

TABLE 10.3 Vapor Pressure of Water at Various Temperatures

Temperature (°C)	Vapor Pressure (atm)
15.0	0.01683
17.0	0.01912
19.0	0.02168
21.0	0.02454
23.0	0.02772
25.0	0.03126
30.0	0.04187
50.0	0.12170

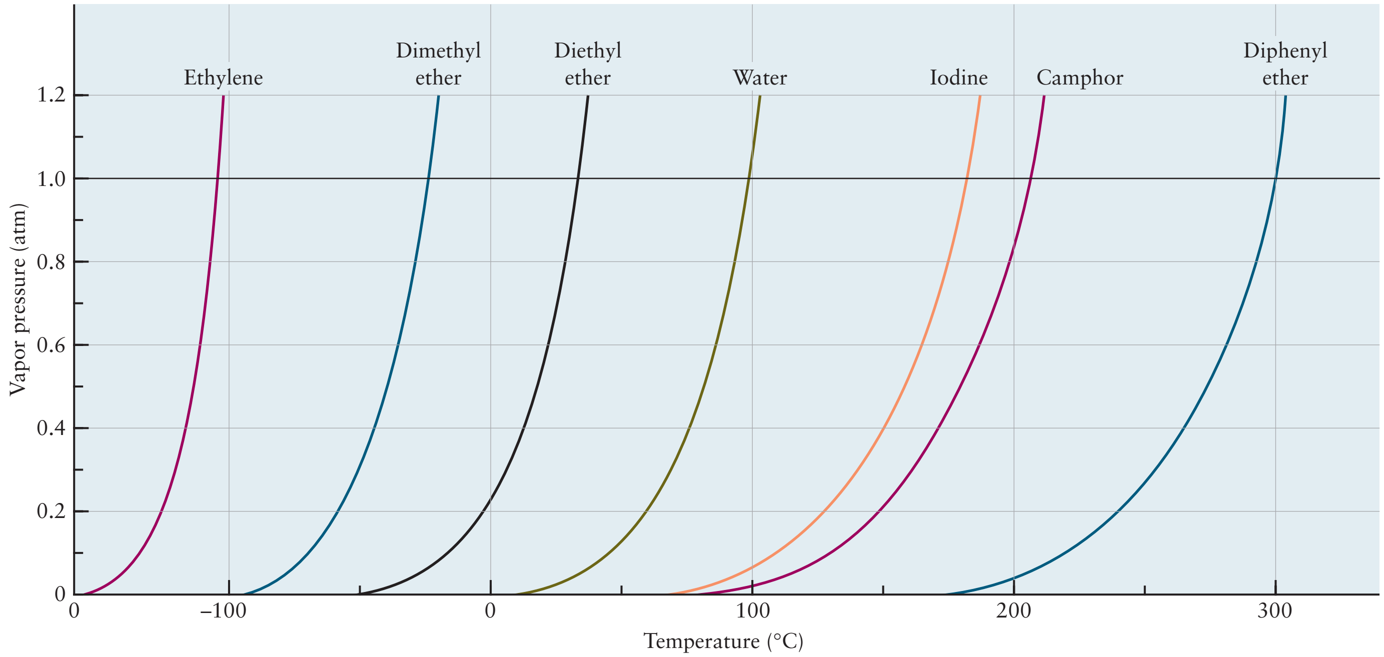


FIGURE 10.17 The vapor pressure of a solid or liquid depends strongly on temperature. The temperature at which the vapor pressure becomes 1 atm defines the normal boiling point of a liquid and the normal sublimation point of a solid.

Phase equilibrium is a *dynamic* process that is quite different from the static equilibrium achieved as a marble rolls to a stop after being spun into a bowl. In the equilibrium between liquid water and water vapor, the partial pressure levels off, not because evaporation and condensation stop, but because at equilibrium their rates become the same. The properties of a system at equilibrium are independent of the direction from which equilibrium is approached, a conclusion that can be drawn by observing the behavior of the liquid-vapor system. If we inject enough water vapor into the empty flask so that initially the pressure of the vapor is *above* the vapor pressure of liquid water, $P_{\text{vap}}(H_2O)$, then liquid water will condense until the same equilibrium vapor pressure is achieved (0.03126 atm at 25°C). Of course, if we do not use enough water vapor to exceed a pressure of 0.03126 atm, all the water will remain in the vapor phase and two-phase equilibrium will not be reached.

The presence of water vapor above an aqueous solution has an important practical consequence. If a reaction in aqueous solution generates gases, these gases are "wet," containing water vapor at a partial pressure given by the equilibrium vapor pressure of water at the temperature of the experiment. The amount of gas generated is determined not by the total pressure but by the partial pressure of the gas. Dalton's law (see Section 9.4) must be used to subtract the partial pressure of water as listed in Table 10.3. This correction is significant in quantitative work.

10.5 Phase Transitions

Suppose 1 mol of gaseous sulfur dioxide is compressed at a temperature fixed at 30.0°C. The volume is measured at each pressure, and a graph of volume against pressure is constructed (Fig. 10.18). At low pressures, the graph shows the inverse dependence ($V \propto 1/P$) predicted by the ideal gas law. As the pressure increases, deviations appear because the gas is not ideal. At this temperature, attractive forces dominate; therefore, the volume falls below its ideal gas value and approaches 4.74 L (rather than 5.50 L) as the pressure approaches 4.52 atm.

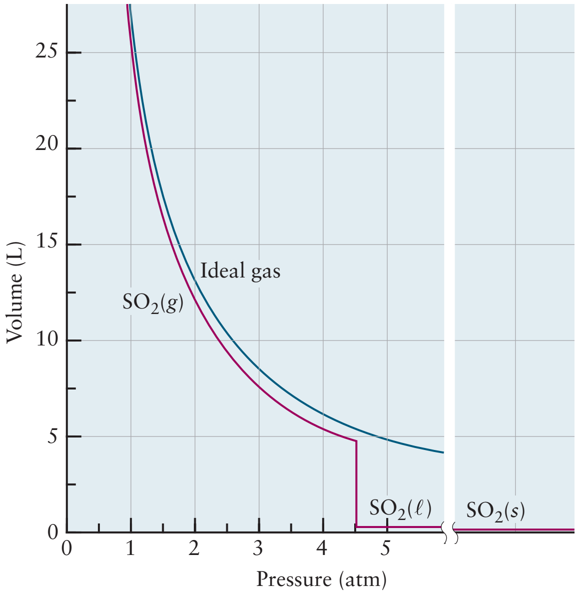


FIGURE 10.18 As 1 mol SO_2 is compressed at a constant temperature of 30°C, the volume at first falls somewhat below its ideal gas value. Then, at 4.52 atm, the volume decreases abruptly as the gas condenses to a liquid. At a much higher pressure, a further transition to the solid occurs.

For pressures up to 4.52 atm, this behavior is quite regular and can be described by the van der Waals equation. At 4.52 atm, something dramatic occurs: The volume decreases abruptly by a factor of 100 and remains small as the pressure is increased further. What has happened? The gas has been liquefied solely by the application of pressure. If the compression of SO_2 is continued, another abrupt (but small) change in volume will occur as the liquid freezes to form a solid.

Condensed phases also arise when the temperature of a gas is reduced at constant pressure. If steam (water vapor) is cooled at 1 atm pressure, it condenses to liquid water at 100°C and freezes to solid ice at 0°C. Liquids and solids form at low temperatures once the attractive forces between molecules become strong enough to overcome the kinetic energy of random thermal motion.

Six **phase transitions** occur among the three states of matter (Fig. 10.19). Solids typically melt to give liquids when they are heated, and liquids boil to give gases. **Boiling** is an extension of evaporation, in which the vapor escapes from the surface only. In boiling, gas bubbles form actively throughout the body of a liquid, and then rise to escape at the surface. Only when the vapor pressure of a liquid exceeds the external pressure can the liquid start to boil. The **boiling point** is the temperature at which the vapor pressure of a liquid equals the external pressure. The external pressure influences boiling points quite strongly; water boils at 25°C if the external pressure is reduced below 0.03126 atm (recall that the vapor pressure of water at 25°C is just this number) but requires a temperature of 121°C to

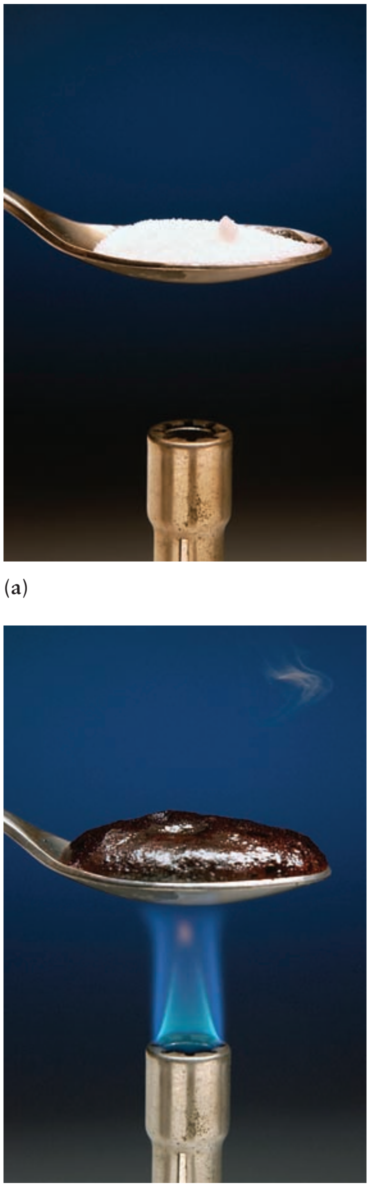
FIGURE 10.19 Direct transitions among all three states of matter not only are possible but are observed in everyday life.

boil under an external pressure of 2.0 atm. At high elevations, the pressure of the atmosphere is lower than 1 atm; thus, water boils at a temperature less than 100°C and food cooks more slowly in boiling water than it would at a lower elevation. In contrast, the use of a pressure cooker increases the boiling temperature of water and speeds the rate at which food is cooked. The **normal boiling point** is defined as the temperature at which the vapor pressure of the liquid equals 1 atm. Figure 10.12 shows that, in general, a lower normal boiling point implies a higher vapor pressure at any fixed temperature (and, therefore, a more volatile liquid).

Melting is the conversion of a solid to the liquid state. The **normal melting point** of a solid is the temperature at which solid and liquid are in equilibrium under a pressure of 1 atm. The normal melting point of ice is 0.00°C, thus liquid water and ice coexist indefinitely (are in equilibrium) at this temperature at a pressure of 1 atm. If the temperature is reduced by even a small amount, then all the water eventually freezes; if the temperature is raised infinitesimally, all the ice eventually melts. The qualifying term *normal* is often omitted in talking about melting points because they depend only weakly on pressure.

It is sometimes possible to overshoot a phase transition, with the new phase appearing only after some delay. An example is the **superheating** of a liquid. Liquid water can reach a temperature somewhat above 100°C if heated rapidly. When vaporization of a superheated liquid does occur, it can be quite violent, with liquid thrown out of the container. Boiling chips (pieces of porous fired clay) may be added to the liquid to avoid this superheating in the laboratory. They help initiate boiling as soon as the normal boiling point is reached, by providing sites where gas bubbles can form. Heating water in a microwave oven in a very clean container can also lead to superheating, and there have been reports of violent boiling resulting in injury as the container is removed from the oven. You should carefully monitor heating times when using a microwave oven to heat water for making coffee or tea. **Supercooling** of liquids below their freezing points is also possible. In careful experiments, supercooled liquid water has been studied at temperatures below −30°C (at atmospheric pressure).

Many materials react chemically when heated, before they have a chance to melt or boil. Substances whose chemical identities change before their physical state changes do not have normal melting or boiling points. For example, sucrose (table sugar) melts but quickly begins to darken and eventually chars (Fig. 10.20). Temperatures high enough to overcome the intermolecular attractions in sugar are also sufficient to break apart the sugar molecules themselves.


(a)

(b)

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FIGURE 10.20 When sugar (a) is heated, it melts and simultaneously decomposes to a dark-colored caramelized mixture (b).

Intermolecular forces exert strong influences on phase transitions. Data presented in Section 10.3 illustrate the trend that the normal boiling point in a series of liquids increases as the strength of intermolecular forces in the liquids increases. The stronger the intermolecular attractions in a liquid, the lower its vapor pressure at any temperature and the higher its temperature must be raised to produce a vapor pressure equal to 1 atm. Melting points depend more strongly on molecular shapes and on the details of the molecular interactions than do boiling points. Consequently, their variation with the strength of the attractive forces is less systematic.

10.6 Phase Diagrams

If the temperature of a substance is held constant and the applied pressure is changed, phase transitions between two phases will be observed at particular pressures. Making the same measurements at a number of different temperatures provides the data necessary to draw the **phase diagram** for that substance—a plot of pressure against temperature that shows the stable state for every pressure–temperature combination. Figure 10.21 shows a sketch of the phase diagram for

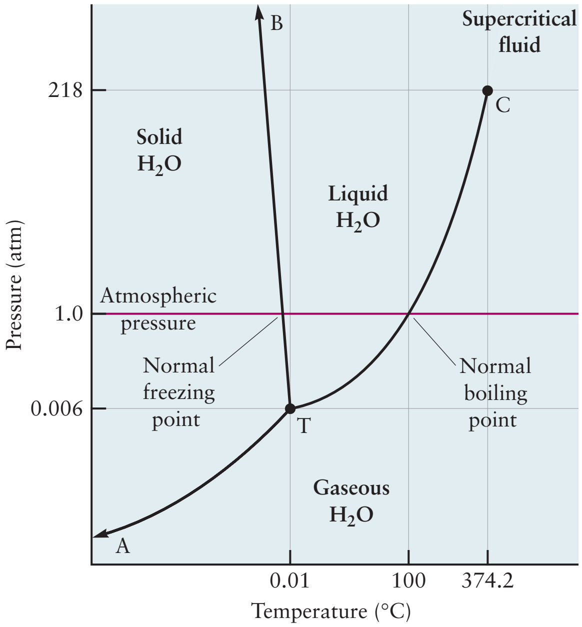

FIGURE 10.21 Phase diagram for water (the pressures and temperatures are not drawn to scale).

water. A great deal of information can be read from such diagrams. For each substance there is a unique combination of pressure and temperature, called the **triple point** (marked "T"), at which the gas, liquid, and solid phases coexist in equilibrium. Extending from the triple point are three lines, each denoting the conditions for the coexistence of two phases at equilibrium. Along the line TA, solid and gas are in equilibrium; along TB, solid and liquid; and along TC, liquid and gas. The regions bounded by these lines represent conditions where only one phase exists.

The gas–liquid coexistence curve extends upward in temperature and pressure from the triple point. This line, stretching from T to C in the phase diagrams, is the vapor pressure curve of the liquid substance, portions of which were shown in Figure 10.17. The gas–liquid coexistence curve does not continue indefinitely, but instead terminates at the **critical point** (point C in Fig. 10.21). Along this coexistence curve there is an abrupt, discontinuous change in the density and other properties from one side to the other. The differences between the properties of the liquid and the gas become smaller as the critical point is approached and disappear altogether at that point. If the substance is placed in a closed container and is gradually heated, a **meniscus** is observed at the boundary between liquid and gas (Fig. 10.22); at the critical point, this meniscus disappears. For pressures above the critical pressure (218 atm for water), it is no longer possible to identify a particular state as gas or liquid. A substance beyond its critical point is called a **supercritical fluid** because the term *fluid* includes both gases and liquids.

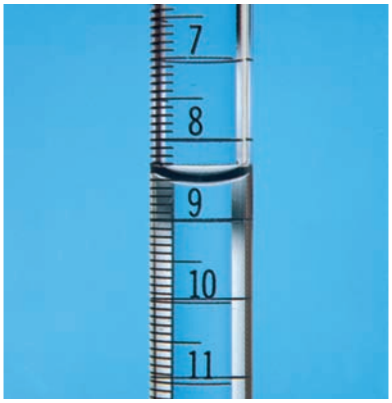

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FIGURE 10.22 When a gas and liquid coexist, the interface between them is clearly visible as a meniscus. The meniscus is useful for reading the volume of a liquid in a buret. It disappears as the critical point is reached.

The liquid–solid coexistence curve does not terminate as the gas–liquid curve does at the critical point, but continues to indefinitely high pressures. In practice, such a curve is almost vertical because large changes in pressure are necessary to change the freezing temperature of a liquid. For most substances, this curve inclines slightly to the right (Figs. 10.23a, b): An increase in pressure increases the freezing point of the liquid. In other words, at constant temperature, an increase in pressure leads to the formation of a phase with higher density (smaller volume), and for most substances, the solid is denser than the liquid. Water and a few other substances are anomalous (see Fig. 10.23c); for them, the liquid–solid coexistence curve slopes up initially to the *left,* showing that an increase in pressure causes the solid to melt. This anomaly is related to the densities of the liquid and solid phases: Ice is less dense than water (which is why ice cubes float on water), so when ice is compressed at 0°C, it melts.

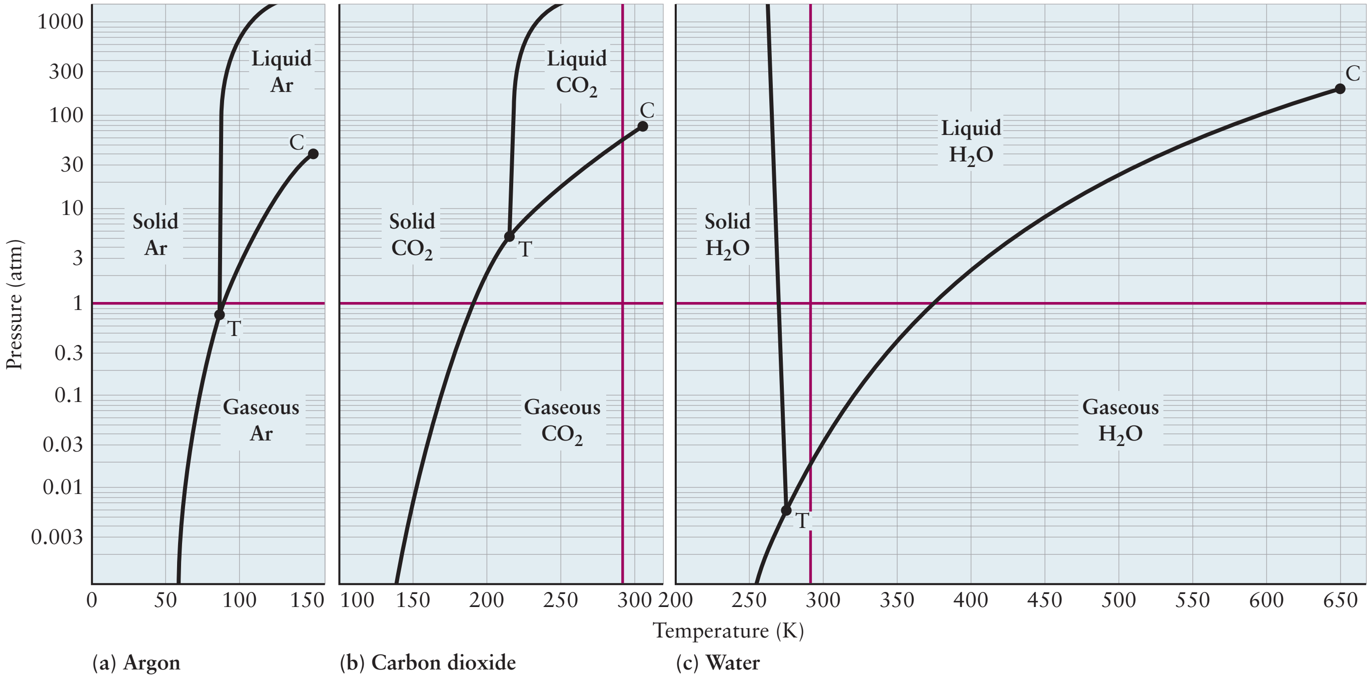

FIGURE 10.23 In these phase diagrams, the pressure increases by a factor of 10 at regular intervals along the vertical axis. This method of graphing allows large ranges of pressure to be plotted. The red horizontal and vertical lines mark a pressure of 1 atm and a temperature of 298.15 K, or 25°C. Their intersection identifies room conditions. Argon and carbon dioxide are gases at room conditions, but water is a liquid. The letter T marks the triple points of the substances, and the letter C marks their critical points. The region of stability of liquid water is larger than that of either carbon dioxide or argon.


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Sublimation of solid carbon dioxide (dry ice). The white clouds are drops of water vapor (moisture in the air) that condense at the low temperatures near the solid surface. Gaseous carbon dioxide itself is transparent.

For most substances, including water (see Fig. 10.23c), atmospheric pressure occurs somewhere between the triple-point pressure and the critical pressure, so in our ordinary experience, all three phases—gas, liquid, and solid—are observed. For a few substances, the triple-point pressure lies *above* $P = 1$ atm, and under atmospheric conditions, there is a direct transition called **sublimation** from solid to gas, without an intermediate liquid state. Carbon dioxide is such a substance (see Fig. 10.23b); its triple-point pressure is 5.117 atm (the triple-point temperature is −56.57°C). Solid CO_2 (dry ice) sublimes directly to gaseous CO_2 at atmospheric pressure. In this respect, it differs from ordinary ice, which melts before it evaporates and sublimes only at pressures below its triple-point pressure, 0.0060 atm. This fact is used in freeze-drying, a process in which foods are frozen and then put in a vacuum chamber at a pressure of less than 0.0060 atm. The ice crystals that formed on freezing then sublime, leaving a dried food that can be reconstituted by adding water.

Many substances exhibit more than one solid phase as the temperature and pressure are varied. At ordinary pressures, the most stable state of carbon is graphite, a rather soft, black solid; but at high enough pressures, the hard, transparent diamond form becomes more stable. That diamonds exist at all at atmospheric pressure is a consequence of how slowly they convert to graphite (we study the graphite-diamond case more thoroughly in our discussions of thermodynamics and spontaneous processes in Chapter 14). Below 13.2°C (and at atmospheric pressure), elemental tin undergoes a slow transformation from the metallic white form to a powdery gray form, a process referred to as "tin disease." This has caused the destruction of tin organ pipes in unheated buildings. No fewer than nine solid forms of ice are known, some of which exist only over a limited range of temperatures and pressures.

EXAMPLE 10.3

Consider a sample of argon held at $P = 600$ atm, $T = 100$ K in Figure 10.23a.

(a) What phase(s) is (are) present at equilibrium?

(b) Suppose the argon originally held at $P = 600$ atm, $T = 100$ K is heated at constant pressure. What happens?

(c) Describe a procedure to convert all the argon to gas without changing the temperature.

SOLUTION

(a) Because this point lies on the liquid–solid coexistence curve, both liquid and solid phases are present.

(b) An increase in temperature at constant pressure corresponds to a movement to the right in the figure, and the solid argon melts to a pure liquid.

(c) If the pressure is reduced sufficiently at constant temperature (below the triple-point pressure of 0.75 atm, for example) the argon will be converted completely to gas.

Related Problems: 43, 44, 45, 46, 47, 48, 49, 50, 51, 52

CHAPTER SUMMARY

The kinetic molecular theory of matter asserts that the macroscopic properties of a gas, liquid, or solid are determined by the number density of its molecules and the nature and strength of the forces between molecules. Intermolecular forces originate in the structures of the molecules and can be calculated from the Coulomb interactions among all the charged particles comprising the molecule. These forces give rise to potential energy between molecules, in magnitudes determined by the distance between the molecules. The repulsive and attractive forces are both included in potential energy functions, and their relative influence shown for each value of intermolecular separation. The same intermolecular forces that cause gas imperfection lead to the formation of liquids and solids. The three phases or states of matter can coexist in equilibrium. On the microscopic level, phase equilibrium is a dynamical balance in which each phase gains and loses molecules from the other phase at the same rate.

CUMULATIVE EXERCISE

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Elemental bismuth.

Bismuth

Bismuth is a rather rare element in the earth's crust, but its oxides and sulfides appear at sufficient concentrations as impurities in lead and copper ores to make its recovery from these sources practical. Annual production of bismuth amounts to several million kilograms worldwide. Although elemental bismuth is a metal, its electrical conductivity is quite poor and it is relatively brittle. The major uses of bismuth arise from its low melting point (271.3°C) and the even lower melting points of its alloys, which range down to 47°C. These alloys are used as temperature sensors in fire detectors and automatic sprinkler systems because, in case of fire, they melt at a well-defined temperature, breaking an electrical connection and triggering an alarm or deluge.

(a) At its normal melting point, the density of solid bismuth is 9.73 g cm^{-3} and that of liquid bismuth is 10.05 g cm^{-3}. Does the volume of a sample of bismuth increase or decrease on melting? Does bismuth more closely resemble water or argon (see Fig. 10.23) in this regard?

(b) Since 1450 (10 years after Gutenberg), bismuth alloys have been used to cast metal type for printing. Explain why those alloys that share the melting behavior of bismuth discussed in part (a) would be especially useful for this application.

(c) A sample of solid bismuth is held at a temperature of 271.0°C and compressed. What will be observed?

(d) The vapor pressure of liquid bismuth has been measured to be 5.0 atm at a temperature of 1850°C. Does its normal boiling point lie above or below this temperature?

(e) At 1060°C, the vapor pressure of liquid bismuth is 0.013 atm. Calculate the number of bismuth atoms per cubic centimeter at equilibrium in the vapor above liquid bismuth at this temperature.

(f) The normal boiling point of liquid tin is 2270°C. Do you predict that liquid tin will be more volatile or less volatile than liquid bismuth at 1060°C?

(g) Bismuth forms two fluorides: BiF_3 and BiF_5. As is usually the case, the compound with the metal in the lower oxidation state has more ionic character, whereas that with the metal in the higher oxidation state has more covalent (molecular) character. Predict which bismuth fluoride will have the higher boiling point.

(h) Will AsF_5 have a higher or a lower normal boiling point than BiF_5?

Answers

(a) Bismuth resembles water in that its volume decreases on melting.

(b) The volume of bismuth increases on freezing; therefore, as the liquid alloy is cast, it fits tightly into its mold rather than shrinking away from the mold as most other metals do. This gives a more sharply defined metal type.

(c) The bismuth will melt.

(d) Its normal boiling point lies below this temperature.

(e) 7.2×10^{16} atoms cm^{-3}

(f) Liquid tin will be less volatile.

(g) BiF_3 will have the higher boiling point; in fact, BiF_3 boils at 900°C and BiF_5 boils at 230°C.

(h) It will have a lower normal boiling point.

CHAPTER REVIEW

The bulk properties of gases, liquids, and solids are defined by their methods of measurement.

- Their magnitudes depend on the structure of the molecules, the forces between the molecules, and the average distance between molecules.
- Molar volume: the volume per mole of a substance
  Ideal gases at standard temperature and pressure $V_m = 22.4 \text{ L mol}^{-1}$
  Liquids and solids: V_m = molar mass/density, typically 10 – 100 cm^3 mol^{-1}
- Compressibility: fractional decrease in volume per unit increase in pressure
  Large for gases
  Small for liquids and solids

- Thermal expansion: fractional increase in volume per 1 K rise in temperature
  Same value for all gases at a given temperature
  Typical values for solids and liquids are of the order $\Delta V/V = 10^{-3}$/K
- Fluidity and rigidity: response to externally applied force (stress)
  Fluids flow, in amount determined by coefficient of viscosity
  Solids do not flow but show rigidity and mechanical strength
- Diffusion: the rate at which molecules of one substance move through the bulk of another substance.
  Quite slow in solids, faster in liquids, rapid in gases
- Surface tension: the energy required to increase the surface area of a liquid. Materials with high surface tensions readily form spherical drops, which have the highest possible surface area to volume ratio.

Intermolecular forces are determined by the structure of the molecules involved.

- Except for van der Waals forces, all intermolecular forces are *electrostatic*. They originate in the Coulomb interactions among all the charged particles in the molecules, and their magnitudes can be calculated from Coulomb's Law when we take proper account of the molecular structures.
- Ionic forces are the strongest and act over the longest distances (range). Their magnitude is easily calculated from Coulomb's Law. They are the dominant force in ionic compounds, which most commonly appear as solids but may be gases or molten salts.
- Ion–dipole forces act between ions and molecules with permanent dipole moments and are next strongest after ionic forces. They are relatively long ranged and are important in ionic solutions.
- Dipole–dipole forces act between neutral molecules that have permanent dipole moments. They are relatively weak and short ranged; the potential energy between two dipoles falls off as $1/R^3$.
- Induced dipole forces arise when an ion induces a dipole in a nonpolar atom or molecule and is then attracted to the opposite charge induced.
- Induced dipole–induced dipole forces arise between neutral nonpolar atoms or molecules and are the only source of attractive forces in substances such as Ar.
- Repulsive forces arise when two atoms or molecules are so close together that their respective electron clouds begin to interfere and overwhelm the attractive forces.

Intermolecular forces in liquids in general are described by the categories discussed above. In addition, hydrogen bonding occurs in substances where H is covalently bonded to N, O, or F.

- Trends in the boiling points of hydrides reveal the special nature of intermolecular forces when H is bonded to N, O, or F. The attractive forces are much stronger than normal dipole–dipole forces, and the orientation of the bond is linear, with the hydrogen located between the two heavy atoms. Hydrogen bonds are 2 to 5 times stronger than dipole–dipole interactions.
- Water has special properties that arise from hydrogen bonding.
  Boiling point is about 150 K higher than would occur without H-bonds.
  Solid is less dense than liquid due to a symmetrical, open, H-bonded network.

Matter is organized into phases, which may be in equilibrium with each other.

- Liquids, solids, and gases are the three normal phases of matter.
- Supercritical fluids and plasmas (ionized gases) are states of matter that appear under specialized conditions and have exotic properties.
- Two or more phases can coexist under given conditions of temperature and pressure.

- Transitions between phases include: evaporation and condensation (liquid to gas and reverse), melting and freezing (liquid to solid and reverse) and sublimation and condensation (solid to gas and reverse).
- Phase equilibria are dynamic events; molecules are constantly shuttling back and forth between phases but with equal rates so that no *macroscopic* changes are observed.

Phase diagrams describe the phases of a substance that exist under various combinations of temperature and pressure in a graphical representation.

- Pressure is plotted on the y-axis and temperature along the x-axis.
- Pressure and temperature conditions under which two phases coexist lie along the *coexistence curves* that divide the two phases.
- The one condition under which three phases can coexist is marked by a single point, the *triple point,* T.
- Above a certain temperature and pressure, marked by the *critical point,* a single *supercritical fluid* exists; its properties are markedly different from normal gases or liquids.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Relate trends in values of bulk properties to the strength and range of intermolecular forces (Section 10.1, Problems 1–12).
2. Relate magnitudes and distance dependence of intermolecular forces to the structure of molecules (Section 10.2, Problems 13–20).
3. Describe the effects of different kinds of intermolecular forces on properties of liquids (Section 10.3, Problems 21–30).
4. Discuss the evidence that phase equilibrium is a dynamic process at the molecular level (Section 10.4, Problems 31–38).
5. Describe the effects of different kinds of intermolecular forces on phase transitions (Section 10.5, Problems 39–42).
6. Sketch the pressure–temperature phase diagram for a typical substance and identify the lines, areas, and singular points (Section 10.6, Problems 43–52).

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

Bulk Properties of Gases, Liquids, and Solids: Molecular Interpretation

1. A substance is nearly nonviscous and quite compressible, and it has a large coefficient of thermal expansion. Is it most likely to be a solid, a liquid, or a gas?

2. A substance is viscous, nearly incompressible, and not elastic. Is it most likely to be a solid, a liquid, or a gas?

3. A sample of volume 258 cm^3 has a mass of 2.71 kg.
   (a) Is the material gaseous or condensed?
   (b) If the molar mass of the material is 108 g mol^{-1}, calculate its molar volume.

4. A sample of volume 18.3 L has a mass of 57.9 g.
   (a) Is the material gaseous or condensed?
   (b) If the molar mass of the material is 123 g mol^{-1}, calculate its molar volume.

5. Heating a sample of matter from 20°C to 40°C at constant pressure causes its volume to increase from 546.0 to 547.6 cm^3. Classify the material as a nearly ideal gas, a nonideal gas, or condensed.

6. Cooling a sample of matter from 70°C to 10°C at constant pressure causes its volume to decrease from 873.6 to 712.6 cm^3. Classify the material as a nearly ideal gas, a nonideal gas, or condensed.

7. At 1.00 atm pressure and a temperature of 25°C, the volume of 1.0 g water is 1.0 mL. At the same pressure and a temperature of 101°C, the volume of 1.0 g water is nearly 1700 times larger. Give the reason for this large change in volume.

8. Doubling the absolute temperature of a gas essentially doubles its volume at constant pressure. Doubling the temperature of many metals, however, often increases their volumes by only a few percent. Explain.

9. Will solid sodium chloride be harder (that is, more resistant to indentation) or softer than solid carbon tetrachloride? Explain.

10. Will the surface tension of molten sodium chloride be higher than or lower than that of carbon tetrachloride? Explain.

11. Do you expect that the diffusion constant will increase or decrease as the density of a liquid is increased (by compressing it) at constant temperature? Explain. What will happen to the diffusion constant of a gas and a solid as the density increases?

12. Do you anticipate that the diffusion constant will increase as the temperature of a liquid increases at constant pressure? Why or why not? Will the diffusion constant increase with temperature for a gas and a solid? Explain.

Intermolecular Forces: Origins in Molecular Structure

13. Compare ion–dipole forces with induced dipole forces. In what ways are they similar and different? Give an example of each.

14. Compare dipole–dipole forces with dispersion forces. In what ways are they similar and different? Give an example of each.

15. Name the types of attractive forces that will contribute to the interactions among atoms, molecules, or ions in the following substances. Indicate the one(s) you expect to predominate.
(a) KF (b) HI (c) Rn (d) N_2

16. Name the types of attractive forces that will contribute to the interactions among atoms, molecules, or ions in the following substances. Indicate the one(s) you expect to predominate.
(a) Ne (b) ClF (c) F_2 (d) $BaCl_2$

17. Predict whether a sodium ion will be most strongly attracted to a bromide ion, a molecule of hydrogen bromide, or an atom of krypton.

18. Predict whether an atom of argon will be most strongly attracted to another atom of argon, an atom of neon, or an atom of krypton.

19. (a) Use Figure 10.9 to estimate the length of the covalent bond in Cl_2 and the length of the ionic bond in K^+Cl^-. **Note:** The latter corresponds to the distance between the atoms in an isolated single molecule of K^+Cl^-, not in KCl(*s*) (solid potassium chloride).

(b) A book states, "The shorter the bond, the stronger the bond." What features of Figure 10.9 show that this is not always true?

20. True or false: Any two atoms held together by nonbonded attractions must be farther apart than any two atoms held together by a chemical bond. Explain.

Intermolecular Forces in Liquids

21. Under room conditions, fluorine and chlorine are gases, bromine is a liquid, and iodine is a solid. Explain the origin of this trend in the physical state of the halogens.

22. The later halogens form pentafluorides: ClF_5, BrF_5, and IF_5. At 0°C, one of these is a solid, one a liquid, and one a gas. Specify which is which, and explain your reasoning.

23. List the following substances in order of increasing normal boiling points, T_b, and explain your reasoning: NO, NH_3, Ne, RbCl.

24. List the following substances in order of increasing normal boiling points, T_b, and explain your reasoning: SO_2, He, HF, CaF_2, Ar.

25. As a vapor, methanol exists to an extent as a tetramer, $(CH_3OH)_4$, in which four CH_3OH molecules are held together by hydrogen bonds. Propose a reasonable structure for this tetramer.

26. Hypofluorous acid (HOF) is the simplest possible compound that allows comparison between fluorine and oxygen in their abilities to form hydrogen bonds. Although F attracts electrons more strongly than O, solid HOF unexpectedly contains no $H \cdots F$ hydrogen bonds! Draw a proposed structure for chains of HOF molecules in the crystalline state. The bond angle in HOF is 101 degrees.

27. Hydrazine (N_2H_4) is used as a reducing agent and in the manufacture of rocket fuels. How do you expect its boiling point to compare with that of ethylene (C_2H_4)?

28. Hydrogen peroxide (H_2O_2) is a major industrial chemical that is produced on a scale approaching 10^9 kg per year. It is widely used as a bleach and in chemical manufacturing processes. How do you expect its boiling point to compare with those of fluorine (F_2) and hydrogen sulfide (H_2S), two substances with molar masses comparable with that of hydrogen peroxide?

29. A flask contains 1.0 L (1.0 kg) of room-temperature water. Calculate the number of possible hydrogen bonds among the water molecules present in this sample. Each water molecule can accept two hydrogen bonds and also furnish the H atoms for two hydrogen bonds.

30. What is the maximum number of hydrogen bonds that can be formed in a sample containing 1.0 mol (N_0 molecules) liquid HF? Compare with the maximum number that can form in 1.0 mol liquid water.

Phase Equilibrium

31. Hydrogen at a pressure of 1 atm condenses to a liquid at 20.3 K and solidifies at 14.0 K. The vapor pressure of liquid hydrogen is 0.213 atm at 16.0 K. Calculate the volume of 1.00 mol H_2 vapor under these conditions and compare it with the volume of 1.00 mol H_2 at standard temperature and pressure.

32. Helium condenses to a liquid at 4.224 K under atmospheric pressure and remains a liquid down to the absolute zero of temperature. (It is used as a coolant to reach very low temperatures.) The vapor pressure of liquid helium at 2.20 K is 0.05256 atm. Calculate the volume occupied by 1.000 mol helium vapor under these conditions and compare it with the volume of the same amount of helium at standard temperature and pressure.

33. The vapor pressure of liquid mercury at 27°C is 2.87×10^{-6} atm. Calculate the number of Hg atoms per cubic centimeter in the "empty" space above the top of the column of mercury in a barometer at 27°C.

34. The tungsten filament in an incandescent lightbulb ordinarily operates at a temperature of about 2500°C. At this temperature, the vapor pressure of solid tungsten is 7.0×10^{-9} atm. Estimate the number of gaseous tungsten atoms per cubic centimeter under these conditions.

35. Calcium carbide reacts with water to produce acetylene (C_2H_2) and calcium hydroxide. The acetylene is collected over water at 40.0°C under a total pressure of 0.9950 atm. The vapor pressure of water at this temperature is 0.0728 atm. Calculate the mass of acetylene per liter of "wet" acetylene collected in this way, assuming ideal gas behavior.

36. A metal reacts with aqueous hydrochloric acid to produce hydrogen. The hydrogen (H_2) is collected over water at 25°C under a total pressure of 0.9900 atm. The vapor pressure of water at this temperature is 0.0313 atm. Calculate the mass of hydrogen per liter of "wet" hydrogen above the water, assuming ideal gas behavior.

37. Carbon dioxide is liberated by the reaction of aqueous hydrochloric acid with calcium carbonate:

$$CaCO_3(s) + 2\,H^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(\ell)$$

A volume of 722 mL $CO_2(g)$ is collected over water at 20°C and a total pressure of 0.9963 atm. At this temperature, water has a vapor pressure of 0.0231 atm. Calculate the mass of calcium carbonate that has reacted, assuming no losses of carbon dioxide.

38. When an excess of sodium hydroxide is added to an aqueous solution of ammonium chloride, gaseous ammonia is produced:

$$NaOH(aq) + NH_4Cl(aq) \longrightarrow NaCl(aq) + NH_3(g) + H_2O(\ell)$$

Suppose 3.68 g ammonium chloride reacts in this way at 30°C and a total pressure of 0.9884 atm. At this temperature, the vapor pressure of water is 0.0419 atm. Calculate the volume of ammonia saturated with water vapor that will be produced under these conditions, assuming no leaks or other losses of gas.

Phase Transitions

39. High in the Andes, an explorer notes that the water for tea is boiling vigorously at a temperature of 90°C. Use Figure 10.17 to estimate the atmospheric pressure at the altitude of the camp. What fraction of the earth's atmosphere lies below the level of the explorer's camp?

40. The total pressure in a pressure cooker filled with water increases to 4.0 atm when it is heated, and this pressure is maintained by the periodic operation of a relief valve. Use Figure 10.23c to estimate the temperature of the water in the pressure cooker.

41. Iridium melts at a temperature of 2410°C and boils at 4130°C, whereas sodium melts at a temperature of 97.8°C and boils at 904°C. Predict which of the two molten metals has the larger surface tension at its melting point. Explain your prediction.

42. Aluminum melts at a temperature of 660°C and boils at 2470°C, whereas thallium melts at a temperature of 304°C and boils at 1460°C. Which metal will be more volatile at room temperature?

Phase Diagrams

43. At its melting point (624°C), the density of solid plutonium is 16.24 g cm^{-3}. The density of liquid plutonium is 16.66 g cm^{-3}. A small sample of liquid plutonium at 625°C is strongly compressed. Predict what phase changes, if any, will occur.

44. Phase changes occur between different solid forms, as well as from solid to liquid, liquid to gas, and solid to gas. When white tin at 1.00 atm is cooled below 13.2°C, it spontaneously changes (over a period of weeks) to gray tin. The density of gray tin is *less* than the density of white tin (5.75 g cm^{-3} vs 7.31 g cm^{-3}). Some white tin is compressed to a pressure of 2.00 atm. At this pressure, should the temperature be higher or lower than 13.2°C for the conversion to gray tin to occur? Explain your reasoning.

45. The following table gives several important points on the pressure-temperature diagram of ammonia:

	P (atm)	*T* (K)
Triple point	0.05997	195.42
Critical point	111.5	405.38
Normal boiling point	1.0	239.8
Normal melting point	1.0	195.45

Use this information to sketch the phase diagram of ammonia.

46. The following table gives several important points on the pressure–temperature diagram of nitrogen:

	P (atm)	*T* (K)
Triple point	0.123	63.15
Critical point	33.3978	126.19
Normal boiling point	1.0	77.35
Normal melting point	1.0	195.45

Use this information to sketch the phase diagram of nitrogen. The density of $N_2(s)$ is 1.03 g cm^{-3} and that of $N_2(\ell)$ is 0.808 g cm^{-3}.

47. Determine whether argon is a solid, a liquid, or a gas at each of the following combinations of temperature and pressure (use Fig. 10.23).

(a) 50 atm and 100 K (c) 1.5 atm and 25 K
(b) 8 atm and 150 K (d) 0.25 atm and 120 K

48. Some water starts out at a temperature of 298 K and a pressure of 1 atm. It is compressed to 500 atm at constant temperature, and then heated to 750 K at constant pressure. Next, it is decompressed at 750 K back to 1 atm and finally cooled to 400 K at constant pressure.

(a) What was the state (solid, liquid, or gas) of the water at the start of the experiment?

(b) What is the state (solid, liquid, or gas) of the water at the end of the experiment?

(c) Did any phase transitions occur during the four steps described? If so, at what temperature and pressure did they occur? (*Hint:* Trace out the various changes on the phase diagram of water [see Fig. 10.23].)

49. The vapor pressure of solid acetylene at −84.0°C is 760 torr.

(a) Does the triple-point temperature lie above or below −84.0°C? Explain.

(b) Suppose a sample of solid acetylene is held under an external pressure of 0.80 atm and heated from 10 to 300 K. What phase change(s), if any, will occur?

50. The triple point of hydrogen occurs at a temperature of 13.8 K and a pressure of 0.069 atm.

(a) What is the vapor pressure of solid hydrogen at 13.8 K?

(b) Suppose a sample of solid hydrogen is held under an external pressure of 0.030 atm and heated from 5 to 300 K. What phase change(s), if any, will occur?

51. The density of nitrogen at its critical point is 0.3131 g cm^{-3}. At a very low temperature, 0.3131 g solid nitrogen is sealed into a thick-walled glass tube with a volume of 1.000 cm^3. Describe what happens inside the tube as the tube is warmed past the critical temperature, 126.19 K.

52. At its critical point, ammonia has a density of 0.235 g cm^{-3}. You have a special thick-walled glass tube that has a 10.0-mm outside diameter, a wall thickness of 4.20 mm, and a length of 155 mm. How much ammonia must you seal into the tube if you wish to observe the disappearance of the meniscus as you heat the tube and its contents to a temperature higher than 132.23°C, the critical temperature?

ADDITIONAL PROBLEMS

53. Would you classify candle wax as a solid or a liquid? What about rubber? Discuss.

* **54.** When a particle diffuses, its *mean-square displacement* in a time interval Δt is $6D\Delta t$, where D is the diffusion constant. Its *root-mean-square displacement* is the square root of this (recall the analogous root-mean-square speed from Section 9.5). Calculate the root-mean-square displacement at 25°C after 1.00 hour of (a) an oxygen molecule in air ($D = 2.1 \times 10^{-5}\ \text{m}^2\ \text{s}^{-1}$), (b) a molecule in liquid water ($D = 2.26 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}$), and (c) an atom in solid sodium ($D = 5.8 \times 10^{-13}\ \text{m}^2\ \text{s}^{-1}$). Note that for solids with melting points higher than sodium, the diffusion constant can be many orders of magnitude smaller.

55. Liquid hydrogen chloride will dissolve many ionic compounds. Diagram how molecules of hydrogen chloride tend to distribute themselves about a negative ion and about a positive ion in such solutions.

* **56.** Section 9.7 explains that the van der Waals constant b (with units of L mol^{-1}) is related to the volume per molecule in the liquid, and thus to the sizes of the molecules. The combination of van der Waals constants a/b has units of L atm mol^{-1}. Because the liter atmosphere is a unit of energy (1 L atm = 101.325 J), a/b is proportional to the energy per mole for interacting molecules, and thus to the strength of the attractive forces between molecules, as shown in Figure 10.9. By using the van der Waals constants in Table 9.3, rank the following attractive forces from strongest to weakest: N_2, H_2, SO_2, and HCl.

57. Describe how the average kinetic and potential energies per mole change as a sample of water is heated from 10 to 1000 K at a constant pressure of 1 atm.

58. As a sample of water is heated from 0.0°C to 4.0°C, its density increases from 0.99987 to 1.00000 g cm^{-3}. What can you conclude about the coefficient of thermal expansion of water in this temperature range? Is water unusual in its behavior? Explain.

59. At 25°C, the equilibrium vapor pressure of water is 0.03126 atm. A humidifier is placed in a room of volume 110 m^3 and is operated until the air becomes saturated with water vapor. Assuming that no water vapor leaks out of the room and that initially there was no water vapor in the air, calculate the number of grams of water that have passed into the air.

60. The text states that at 1000°C, the vapor pressure of tungsten is 2×10^{-25} atm. Calculate the volume occupied per tungsten *atom* in the vapor under these conditions.

61. You boil a small quantity of water inside a 5.0-L metal can. When the can is filled with water vapor (and all air has been expelled), you quickly seal the can with a screw-on cap and remove it from the source of heat. It cools to 60°C and most of the steam condenses to liquid water. Determine the pressure inside the can. (*Hint:* Refer to Fig. 10.17.)

* **62.** The air over an unknown liquid is saturated with the vapor of that liquid at 25°C and a total pressure of 0.980 atm. Suppose that a sample of 6.00 L of the saturated air is collected and the vapor of the unknown liquid is removed from that sample by cooling and condensation. The pure air remaining occupies a volume of 3.75 L at −50°C and 1.000 atm. Calculate the vapor pressure of the unknown liquid at 25°C.

63. If it is true that all solids and liquids have vapor pressures, then at sufficiently low external pressures, every substance should start to boil. In space, there is effectively zero external pressure. Explain why spacecraft do not just boil away as vapors when placed in orbit.

64. Butane-fueled cigarette lighters, which give hundreds of lights each, typically contain 4 to 5 g butane (C_4H_{10}), which is confined in a 10-mL plastic container and exerts a pressure of 3.0 atm at room temperature (25°C). The butane boils at −0.5°C under normal pressure. Butane lighters have been known to explode during use, inflicting serious injury. A person hoping to end such accidents suggests that there be less butane placed in the lighters so that the pressure inside them does not exceed 1.0 atm. Estimate how many grams of butane would be contained in such a lighter.

65. A cooling bath is prepared in a laboratory by mixing chunks of solid CO_2 with ethanol. $CO_2(s)$ sublimes at −78.5°C to $CO_2(g)$. Ethanol freezes at −114.5°C and boils at +78.4°C. State the temperature of this cooling bath and describe what will be seen when it is prepared under ordinary laboratory conditions.

66. Oxygen melts at 54.8 K and boils at 90.2 K at atmospheric pressure. At the normal boiling point, the density of the liquid is 1.14 g cm^{-3} and the vapor can be approximated as an ideal gas. The critical point is defined by $T_c = 154.6$ K, $P_c = 49.8$ atm, and (density) $d_c = 0.436$ g cm^{-3}. The triple point is defined by $T_t = 54.4$ K, $P_t = 0.0015$ atm, a liquid density equal to 1.31 g cm^{-3}, and a solid density of 1.36 g cm^{-3}. At 130 K, the vapor pressure of the liquid is 17.25 atm. Use this information to construct a phase diagram showing P versus T for oxygen. You need not draw the diagram to scale, but you should give numeric labels to as many points as possible on both axes.

67. It can be shown that if a gas obeys the van der Waals equation, its critical temperature, its critical pressure, and its molar volume at the critical point are given by the equations

$$T_c = \frac{8a}{27Rb} \qquad P_c = \frac{a}{27b^2} \qquad \left(\frac{V}{n}\right)_c = 3b$$

where a and b are the van der Waals constants of the gas. Use the van der Waals constants for oxygen, carbon dioxide, and water (from Table 9.3) to estimate the critical-point properties of these substances. Compare with the observed values given in Figure 10.23 and in Problem 66.

*** 68.** Each increase in pressure of 100 atm decreases the melting point of ice by about 1.0°C.

(a) Estimate the temperature at which liquid water freezes under a pressure of 400 atm.

(b) One possible explanation of why a skate moves smoothly over ice is that the pressure exerted by the skater on the ice lowers its freezing point and causes it to melt. The pressure exerted by an object is the force (its mass × the acceleration of gravity, 9.8 m s^{-2}) divided by the area of contact. Calculate the change in freezing point of ice when a skater with a mass of 75 kg stands on a blade of area 8.0×10^{-5} m^2 in contact with the ice. Is this sufficient to explain the ease of skating at a temperature of, for example, −5°C (23°F)?

*** 69. (a)** Sketch the phase diagram of *temperature* versus *molar volume* for carbon dioxide, indicating the region of each of the phases (gas, liquid, and solid) and the coexistence regions for two phases.

(b) Liquid water has a maximum at 4°C in its curve of density against temperature at $P = 1$ atm, and the solid is less dense than the liquid. What happens if you try to draw a phase diagram of T versus molar volume for water?

70. The critical temperature of HCl is 51°C, lower than that of HF, 188°C, and HBr, 90°C. Explain this by analyzing the nature of the intermolecular forces in each case.

71. The normal boiling points of the fluorides of the second-period elements are as follows: LiF, 1676°C; BeF_2, 1175°C; BF_3, −100°C; CF_4, −128°C; NF_3, −129°C; OF_2, −145°C; F_2, −188°C. Describe the nature of the intermolecular forces in this series of liquids, and account for the trends in boiling point.

CUMULATIVE PROBLEMS

72. At 20°C and a pressure of 1 atm, 1 mol argon gas occupies a volume of 24.0 L. Estimate the van de Waals radius for argon from the onset of the repulsive part of the argon intermolecular potential curve in Figure 9.18, and calculate the fraction of the gas volume that consists of argon atoms.

73. Other things being equal, ionic character in compounds of metals decreases with increasing oxidation number. Rank the following compounds from lowest to highest normal boiling points: AsF_5, SbF_3, SbF_5, F_2.

CHAPTER 11

Solutions

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Dissolution of sugar in water.

Homogeneous systems that contain two or more substances are called **solutions.** Usually, we think of a solution as a liquid that contains some dissolved substance, such as a solid or gas, and we use the term in that sense in most of this chapter. But, solutions of one solid in another are also common, one example being an alloy of gold and silver. In fact, any homogeneous system of two or more substances (liquid, solid, or gas) is a solution. The major component is usually called the **solvent,** and minor components are called the **solutes.** The solvent is regarded as a "carrier" or medium for the solute, which can participate in chemical reactions in the solution or leave the solution through precipitation or evaporation. Throughout this chapter, it is helpful to keep in mind one guiding question: How are the reactions and the properties of the pure solute modified when it is dispersed in the solvent?

Description of these phenomena requires quantitative specifications of the amount of solute in the solution, or the *composition* of the solution. Solutions are formed by mixing two or more pure substances whose molecules interact directly in the mixed state. Molecules experience new intermolecular forces in moving from pure solute or solvent into the mixed state. The magnitude of these changes influences both the ease of formation and the stability of a solution.

Chemical reactions are frequently carried out in solution, and their description requires modifications to the rules of stoichiometry described in Chapter 2. We illustrate these modified rules by the important analytical techniques of titration in acid–base and oxidation–reduction reactions.

Just like pure substances, solutions can be in *phase equilibrium* with gases, solids, or other liquids. These equilibria frequently show interesting effects that depend on the molecular weight of the solute.

This chapter begins by explaining how the composition of solutions is defined and how solutions are prepared. It is important to master these concepts, because the properties and behavior of solutions are determined by their composition. With this background, we give quantitative descriptions of chemical reactions and phase equilibria in solutions, and relate these events to the nature of the species in the solution.

11.1 Composition of Solutions

Several measures are used to specify the composition of a solution. **Mass percentage** (colloquially called weight percentage), frequently used in everyday applications, is defined as the percentage by mass of a given substance in the solution. In quantitative chemistry, the most useful measures of composition are mole fraction, molarity, and molality.

The **mole fraction** of a substance in a mixture is the number of moles of that substance divided by the total number of moles present. This term was introduced in the discussion of gas mixtures and Dalton's law (see Section 9.4). In a binary mixture containing n_1 mol of species 1 and n_2 mol of species 2, the mole fractions X_1 and X_2 are

$$X_1 = \frac{n_1}{n_1 + n_2} \qquad [11.1a]$$

$$X_2 = \frac{n_2}{n_1 + n_2} = 1 - X_1 \qquad [11.1b]$$

The mole fractions of all the species present must add up to 1. When a clear distinction can be made between solvent and solutes, the label 1 denotes the solvent and higher numbers are given to the solutes. If comparable amounts of two liquids such as water and alcohol are mixed, the assignment of the labels 1 and 2 is arbitrary.

The **concentration** of a substance is the number of moles per unit volume. The SI units moles per cubic meter are inconveniently large for chemical work, so instead we use the **molarity,** defined as the number of moles of solute per liter of solution:

$$\text{molarity} = \frac{\text{moles solute}}{\text{liters solution}} = \text{mol L}^{-1} \qquad [11.2]$$

M is the abbreviation for "moles per liter." A 0.1 M (read "0.1 molar") solution of HCl has 0.1 mol of HCl (dissociated into ions, as explained later in this chapter) per liter of solution. Molarity is the most common way of specifying the compositions of dilute solutions. For accurate measurements it has the disadvantage of depending slightly on temperature. If a solution is heated or cooled, its volume changes, so the number of moles of solute per liter of solution also changes.

The **molality,** in contrast, involves the ratio of two masses, and so does not depend on temperature. Molality is defined as the number of moles of solute per kilogram of *solvent:*

$$\text{molality} = \frac{\text{moles solute}}{\text{kilograms solvent}} = \text{mol kg}^{-1} \qquad [11.3]$$

Because the density of water is 1.00 g cm^{-3} at 20°C, 1.00 L of water has mass of 1.00×10^3 g, or 1.00 kg. It follows that in a dilute aqueous solution, the number of moles of solute per liter is nearly the same as the number of moles per kilogram of water. Therefore, molarity and molality have nearly equal values. For nonaqueous solutions and concentrated aqueous solutions, this approximate equality is no longer valid.

EXAMPLE 11.1

A solution is prepared by dissolving 22.4 g of $MgCl_2$ in 0.200 L of water. Taking the density of pure water to be 1.00 g cm^{-3} and the density of the resulting solution to be 1.089 g cm^{-3}, calculate the mole fraction, molarity, and molality of $MgCl_2$ in this solution.

SOLUTION

We are given the *mass* of the $MgCl_2$ and the *volume* of the water. The number of moles for each are

$$\text{moles MgCl}_2 = \frac{22.4 \text{ g}}{95.22 \text{ g mol}^{-1}} = 0.235 \text{ mol}$$

$$\text{moles water} = \frac{(0.200 \text{ L})(1000 \text{ cm}^3 \text{ L}^{-1})(1.00 \text{ g cm}^{-3})}{18.02 \text{ g mol}^{-1}}$$

$$= 11.1 \text{ mol}$$

$$\text{mole fraction MgCl}_2 = \frac{0.235 \text{ mol}}{(11.1 + 0.235) \text{ mol}} = 0.0207$$

To calculate the molarity, we must first determine the volume of solution. Its mass is 200 g water + 22.4 g MgCl = 222.4 g, and its density is 1.089 g cm^{-3}, so the volume is

$$\text{volume solution} = \frac{222.4 \text{ g}}{1.089 \text{ g cm}^{-3}} = 204 \text{ cm}^3 = 0.204 \text{ L}$$

$$\text{molarity MgCl}_2 = \frac{0.235 \text{ mol MgCl}_2}{0.204 \text{ L}} = 1.15 \text{ M}$$

$$\text{molality MgCl}_2 = \frac{0.235 \text{ mol MgCl}_2}{0.200 \text{ kg H}_2\text{O}} = 1.18 \text{ mol kg}^{-1}$$

Related Problems: 3, 4

EXAMPLE 11.2

A 9.386 M aqueous solution of sulfuric acid has a density of 1.5091 g cm^{-3}. Calculate the molality, the percentage by mass, and the mole fraction of sulfuric acid in this solution.

SOLUTION

It is convenient to choose 1 L of the solution, whose mass is

$$(1000 \text{ cm}^3)(1.5091 \text{ g cm}^{-3}) = 1509.1 \text{ g} = 1.5091 \text{ kg}$$

One liter contains 9.386 mol H_2SO_4, or

$$9.386 \text{ mol H}_2\text{SO}_4 \times 98.08 \text{ g mol}^{-1} = 920.6 \text{ g H}_2\text{SO}_4$$

The mass of water in this liter of solution is then obtained by subtraction:

$$\text{Mass of water in 1 L of solution} = 1.5091 \text{ kg} - 0.9206 \text{ kg} = 0.5885 \text{ kg}$$

The molality is now directly obtained as

$$\text{Molality H}_2\text{SO}_4 = \frac{9.386 \text{ mol H}_2\text{SO}_4}{0.5885 \text{ kg H}_2\text{O}} = 15.95 \text{ mol kg}^{-1}$$

and the mass percentage is

$$\text{Mass percentage H}_2\text{SO}_4 = \frac{0.9206 \text{ kg}}{1.5091 \text{ kg}} \times 100\% = 61.00\%$$

The number of moles of water is

$$\text{moles H}_2\text{O} = \frac{588.5 \text{ g}}{18.02 \text{ g mol}^{-1}} = 32.66 \text{ mol}$$

so that the mole fraction of H_2SO_4 is

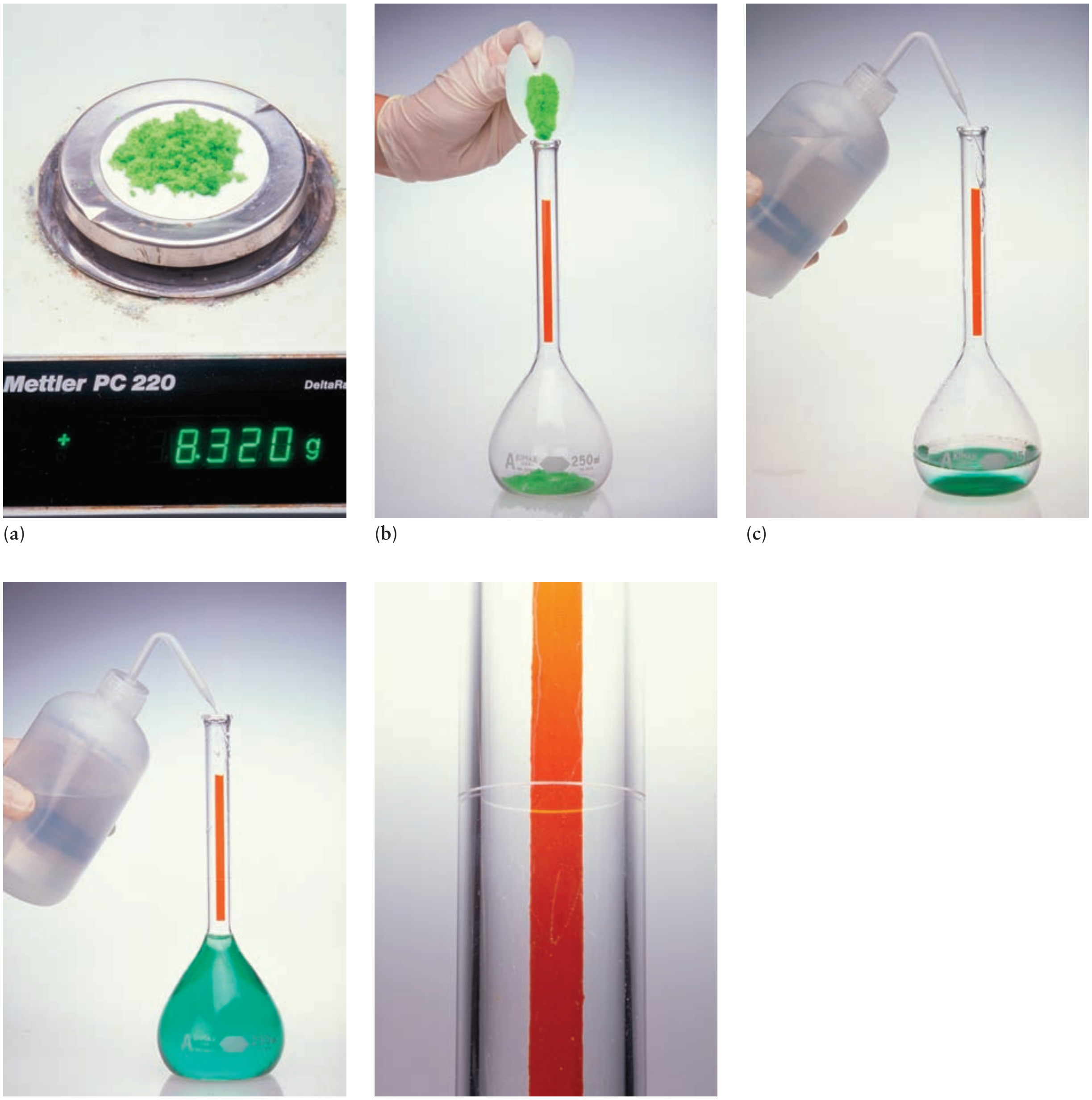
$$\text{Mole fraction H}_2\text{SO}_4 = X_2 = \frac{9.386 \text{ mol}}{9.386 + 32.66 \text{ mol}} = 0.2232$$

Related Problems: 5, 6

Preparation of Solutions

Examples 11.1 and 11.2 show that if a known mass of solute is added to a known volume of solvent, the molarity can be calculated only if the density of the resulting solution is known. If 1 L of solvent is used, the volume of the resulting solution is less than 1 L in some cases and more in others. If a solution is to have a given molarity, it is clearly inconvenient to need to know the solution density. We avoid this problem in practice by dissolving the measured amount of solute in a smaller amount of solvent, then adding solvent continuously until the desired total volume is reached. For accurate work, solutions are prepared in a **volumetric flask,** which has a distinct ring marked around its neck to indicate a carefully calibrated volume (Fig. 11.1). Filling the flask with solvent up to this mark controls the volume of the solution.

Sometimes it may be necessary to prepare a dilute solution of specified concentration from a more concentrated solution of known concentration by adding pure solvent to the concentrated solution. Suppose that the initial concentration (molarity) is c_i and the initial solution volume is V_i. The number of moles of solute is $(c_i \text{ mol L}^{-1})(V_i \text{ L}) = c_iV_i$ mol. This number does not change on dilution to a final



(a) (b) (c) (d) (e)

FIGURE 11.1 To prepare a solution of nickel chloride, $NiCl_2$, with accurately known concentration, weigh out an amount of the solid (a), transfer it to a volumetric flask (b), dissolve it in somewhat less than the required amount of water (c), and dilute to the total volume marked on the neck of the flask (d), (e).
(© Thomson Learning/Charles D. Winters)

solution volume, V_f, because only solvent, and not solute, is being added. Thus, $c_i V_i = c_f V_f$ and the final molarity is

$$c_f = \frac{\text{moles solute}}{\text{final solution volume}} = \frac{c_i V_i}{V_f} \qquad [11.4]$$

This equation can be used to calculate the final concentration after dilution to a given final volume and also to determine what final volume should be used to obtain a given concentration.

EXAMPLE 11.3

(a) Describe how to prepare 0.500 L of a 0.100 M aqueous solution of potassium hydrogen carbonate ($KHCO_3$).

(b) Describe how to dilute this solution to a final concentration of 0.0400 M $KHCO_3$.

SOLUTION

(a)

$$\text{moles solute} = (0.500\ \text{L})(0.100\ \text{mol L}^{-1}) = 0.0500\ \text{mol}$$

$$\text{grams solute} = (0.0500\ \text{mol})(100.12\ \text{g mol}^{-1}) = 5.01\ \text{g}$$

because 100.12 is the molar mass of $KHCO_3$. We would, therefore, dissolve 5.01 g $KHCO_3$ in a small amount of water and dilute the solution to 0.500 L.

(b) Rearranging Equation 11.4 gives

$$V_f = \frac{c_i}{c_f} V_i$$

$$= \left(\frac{0.100\ \text{mol L}^{-1}}{0.0400\ \text{mol L}^{-1}}\right)(0.500\ \text{L}) = 1.25\ \text{L}$$

To achieve this, the solution from part **(a)** is diluted to a total volume of 1.25 L by adding water.

Related Problems: 9, 10

11.2 Nature of Dissolved Species

In the formation of a solution the attractions among the particles in the original phases (solvent-to-solvent and solute-to-solute attractions) are broken up and replaced, at least in part, by new solvent-to-solute attractions. Unlike a compound, a solution has its components present in *variable* proportions and cannot be represented by a chemical formula. Equations for dissolution reactions do not include the solvent as a reactant. They indicate the original state of the solute in parentheses on the left side of the equation and identify the solvent in parentheses on the right side. For example, solid (*s*) sucrose dissolves in water to give an **aqueous** (*aq*) solution of sucrose:

$$C_{12}H_{22}O_{11}(s) \longrightarrow C_{12}H_{22}O_{11}(aq)$$

Although the solute and solvent can be any combination of solid, liquid, and gas phases, liquid water is indisputably the best known and most important solvent. Consequently, we emphasize aqueous solutions in this chapter, but you should always remember that dissolution also occurs in many other solvents. We describe formation of aqueous solutions by considering the intermolecular forces between the solute and water molecules. Because these forces can be quite different for molecular solutes and ionic solutes, we discuss these two cases separately.

Aqueous Solutions of Molecular Species

Molecular substances that have polar molecules are readily dissolved by water. Examples are the sugars, which have the general formula $C_m(H_2O)_n$. Specific cases are sucrose (table sugar), $C_{12}H_{22}O_{11}$; fructose (fruit sugar), $C_6H_{12}O_6$; and ribose, $C_5H_{10}O_5$, a subunit in the biomolecules known as ribonucleic acids. Despite their general formula, the sugars do not contain water molecules, but they do include polar OH (hydroxyl) groups bonded to carbon atoms, which provide sites for hydrogen-bonding interactions with water molecules. These attractions replace the solute–solute interactions, and the individual aquated sugar molecules move off into the solution (Fig. 11.2). Many other molecular substances follow the same pattern, provided they are sufficiently polar. Nonpolar substances, such as carbon tetrachloride, octane, and the common oils and waxes, do not dissolve significantly in water.

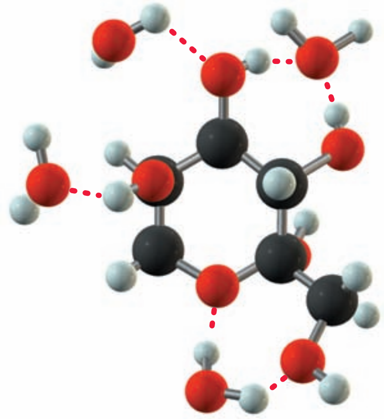


FIGURE 11.2 A molecule of fructose in aqueous solution. Note the attractions between the hydroxyl (O—H) groups of the fructose and molecules of water. The fructose molecule is aquated; the exact number and arrangement of the attached water molecules fluctuate. Also shown is one hydrogen bond between a water molecule and an oxygen atom in the fructose ring.

Aqueous Solutions of Ionic Species (Electrolytes)

Potassium sulfate is an ionic solid that dissolves in water up to 120 g L^{-1} at 25°C; this maximum mass that can be dissolved in 1 L at 25°C is called the **solubility** in water. The chemical equation for this **dissolution reaction** is written as

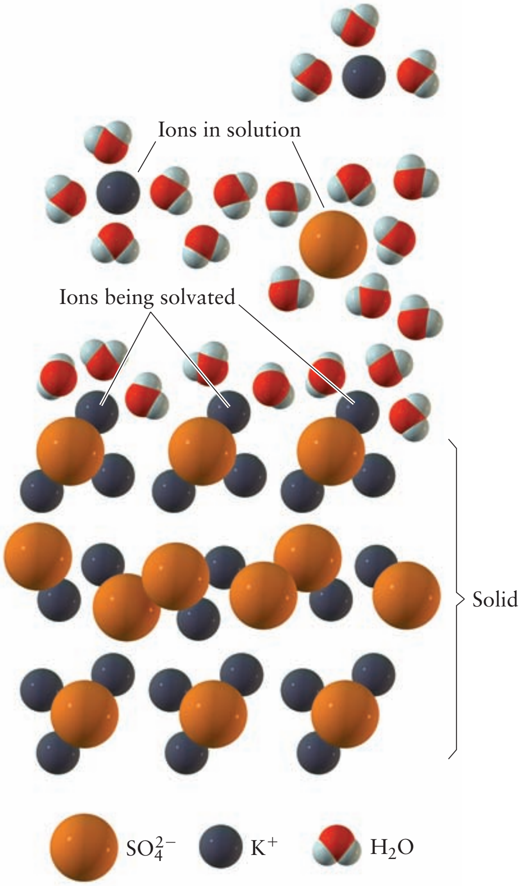
$$K_2SO_4(s) \longrightarrow 2\,K^+(aq) + SO_4^{2-}(aq)$$

The dissolution of ionic species (Fig. 11.3) occurs through the ion–dipole forces described in Section 10.2. Each positive ion in solution is surrounded by water molecules oriented with the negative end of their dipole moments toward the positive ion. Each SO_4^{2-} anion in solution is surrounded by water molecules oriented with the positive end of their dipole moments toward the anion. When a halide such as KCl is dissolved, the anion forms a hydrogen bond with one of the H atoms in a water molecule that places the atoms O—H—Cl nearly in a straight line as described in Section 10.2.

Each ion dissolved in water and its surrounding **solvation shell** of water molecules constitute an entity held together by ion–dipole forces or by hydrogen bonds. These solvated ions can move as intact entities when an electric field is applied (Fig. 11.4). Because the resulting solution is a conductor of electricity, ionic species such as K_2SO_4 are called **electrolytes.**

In Example 11.1, it is important to note that, although the molarity of $MgCl_2$ is 1.15 M, the molarity of Cl^- ions in the solution is twice as large, or 2.30 M, because each formula unit of $MgCl_2$ dissociates to give two Cl^- ions.

FIGURE 11.3 When an ionic solid (in this case, K_2SO_4) dissolves in water, the ions move away from their sites in the solid, where they were attracted strongly by ions of opposite electrical charge. New strong attractions replace those lost as each ion is surrounded by a group of water molecules. In a precipitation reaction, the process is reversed.



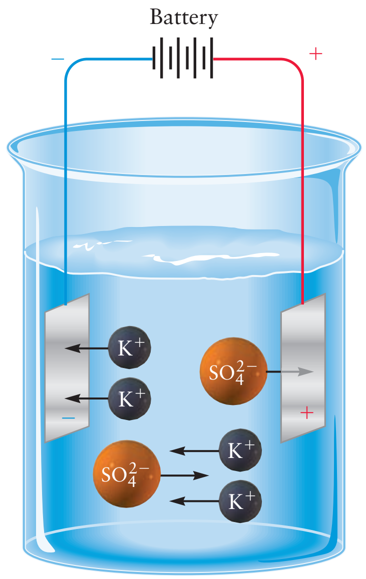


FIGURE 11.4 An aqueous solution of potassium sulfate conducts electricity. When metallic plates (electrodes) charged by a battery are put in the solution, positive ions (K^+) migrate toward the negative plate and negative ions (SO_4^{2-}) migrate toward the positive plate.

Different compounds dissolve to different extents in water. Only a small amount (0.0025 g) of solid barium sulfate dissolves per liter of water at 25°C, according to the following reaction:

$$BaSO_4(s) \longrightarrow Ba^{2+}(aq) + SO_4^{2-}(aq)$$

The near-total insolubility of barium sulfate suggests that mixing a sufficiently large amount of aqueous barium ion with aqueous sulfate ion would cause the reverse reaction to occur and solid barium sulfate would appear. Of course, it is impossible to prepare a solution containing ions of one charge only. Ions of both charges must be present to maintain overall charge neutrality. But it is possible to prepare one solution that contains a soluble barium compound in water (such as barium chloride) and a second solution that contains a soluble sulfate compound in water (such as potassium sulfate). Mixing the two solutions (Fig. 11.5) then produces solid barium sulfate through the following reaction:

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$$

which is called a **precipitation reaction.**

Such precipitation reactions are sometimes written as

$$BaCl_2(aq) + K_2SO_4(aq) \longrightarrow BaSO_4(s) + 2\ KCl(aq)$$

which suggests ionic exchange—that is, the two anions exchange places. This is misleading, because $BaCl_2$, K_2SO_4, and KCl are all dissociated into ions in aqueous solution. It is more accurate to write

$$Ba^{2+}(aq) + 2\ Cl^-(aq) + 2\ K^+(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s) + 2\ K^+(aq) + 2\ Cl^-(aq)$$

The potassium and chloride ions appear on both sides of the equation. They are **spectator ions,** which ensure charge neutrality but do not take part directly in the chemical reaction. Omitting such spectator ions from the balanced chemical equation leads to the **net ionic equation:**

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)$$

A net ionic equation includes only the ions (and molecules) that actually take part in the reaction.

In dissolution and precipitation reactions, ions retain their identities, and in particular, oxidation states do not change. The ions simply exchange the positions they had in a solid (surrounded by other ions) for new positions in solution (surrounded by solvent molecules). They undergo the reverse process in precipitation.


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FIGURE 11.5 A solution of potassium sulfate is being added to one of barium chloride. A cloud of white solid barium sulfate is formed; the potassium chloride remains in solution.

EXAMPLE 11.4

An aqueous solution of sodium carbonate is mixed with an aqueous solution of calcium chloride, and a white precipitate immediately forms. Write a net ionic equation to account for this precipitate.

SOLUTION

Aqueous sodium carbonate contains $Na^+(aq)$ and $CO_3^{2-}(aq)$ ions, and aqueous calcium chloride contains $Ca^{2+}(aq)$ and $Cl^-(aq)$ ions. Mixing the two solutions places $Na^+(aq)$ and $Cl^-(aq)$ ions and also $Ca^{2+}(aq)$ and $CO_3^{2-}(aq)$ ions in contact for the first time. The precipitate forms by the following reaction:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$$

because the other combination of ions leads to sodium chloride, a compound that is known to be soluble in water.

Related Problems: 13, 14

11.3 Reaction Stoichiometry in Solutions: Acid–Base Titrations

Reactions in Solution

Most chemical reactions that occur on the earth's surface, whether in living organisms or among inorganic substances, take place in aqueous solution. Chemical reactions carried out between substances in solution obey the requirements of stoichiometry discussed in Chapter 2, in the sense that the conservation laws embodied in balanced chemical equations are always in force. But here we must apply these requirements in a slightly different way. Instead of a conversion between masses and number of moles, using the molar mass as a conversion factor, the conversion is now between *solution volumes* and number of moles, with the concentration as the conversion factor.

For instance, consider the reaction that is used commercially to prepare elemental bromine from its salts in solution:

$$2\ \mathrm{Br^-}(aq) + \mathrm{Cl_2}(aq) \longrightarrow 2\ \mathrm{Cl^-}(aq) + \mathrm{Br_2}(aq)$$

Suppose there is 50.0 mL of a 0.0600 M solution of NaBr. What volume of a 0.0500 M solution of Cl_2 is needed to react completely with the Br^-? To answer this, find the number of moles of bromide ion present:

$$0.0500\ \mathrm{L} \times (0.0600\ \mathrm{mol\ L^{-1}}) = 3.00 \times 10^{-3}\ \mathrm{mol\ Br^-}$$

Next, use the chemical conversion factor 1 mol of Cl_2 per 2 mol of Br^- to find

$$\text{moles } \mathrm{Cl_2} \text{ reacting} = 3.00 \times 10^{-3}\ \mathrm{mol\ Br^-}\left(\frac{1\ \mathrm{mol\ Cl_2}}{2\ \mathrm{mol\ Br^-}}\right) = 1.50 \times 10^{-3}\ \mathrm{mol\ Cl_2}$$

Finally, find the necessary volume of aqueous chlorine:

$$\frac{1.50 \times 10^{-3}\ \mathrm{mol}}{0.0500\ \mathrm{mol\ L^{-1}}} = 3.00 \times 10^{-2}\ \mathrm{L\ solution}$$

The reaction requires 3.00×10^{-2} L, or 30.0 mL, of the Cl_2 solution. (In practice, an excess of Cl_2 solution would be used to ensure more nearly complete conversion of the bromide ion to bromine.)

The chloride ion concentration after completion of the reaction might also be of interest. Because each mole of bromide ion that reacts gives 1 mol of chloride ion in the products, the number of moles of Cl^- produced is 3.00×10^{-3} mol. The final volume of the solution is 0.0800 L, so the final concentration of Cl^- is

$$[\mathrm{Cl^-}] = \frac{3.00 \times 10^{-3}\ \mathrm{mol}}{0.0800\ \mathrm{L}} = 0.0375\ \mathrm{M}$$

Square brackets around a chemical symbol signify the molarity of that species.

EXAMPLE 11.5

When potassium dichromate is added to concentrated hydrochloric acid, it reacts according to the following chemical equation

$$\mathrm{K_2Cr_2O_7}(s) + 14\ \mathrm{HCl}(aq) \longrightarrow 2\ \mathrm{K^+}(aq) + 2\ \mathrm{Cr^{3+}}(aq) + 8\ \mathrm{Cl^-}(aq) + 7\ \mathrm{H_2O}(\ell) + 3\ \mathrm{Cl_2}(g)$$

producing a mixed solution of chromium(III) chloride and potassium chloride and evolving gaseous chlorine. Suppose that 6.20 g of $K_2Cr_2O_7$ reacts with concentrated HCl, and that the final volume of the solution is 100.0 mL. Calculate the final concentration of $Cr^{3+}(aq)$ and the number of moles of chlorine produced.

SOLUTION

The first step is to convert the mass of $K_2Cr_2O_7$ to moles:

$$\frac{6.20 \text{ g } K_2Cr_2O_7}{294.19 \text{ g mol}^{-1}} = 0.0211 \text{ mol } K_2Cr_2O_7$$

The balanced chemical equation states that 1 mol of $K_2Cr_2O_7$ reacts to give 2 mol of Cr^{3+} and 3 mol of Cl_2. Using these two chemical conversion factors gives

$$\begin{aligned}\text{moles } Cr^{3+} &= 0.0211 \text{ mol } K_2Cr_2O_7\left(\frac{2 \text{ mol } Cr^{3+}}{1 \text{ mol } K_2Cr_2O_7}\right)\\ &= 0.0422 \text{ mol } Cr^{3+}\end{aligned}$$

$$\begin{aligned}\text{moles } Cl_2 &= 0.0211 \text{ mol } K_2Cr_2O_7\left(\frac{3 \text{ mol } Cl_2}{1 \text{ mol } K_2Cr_2O_7}\right)\\ &= 0.0633 \text{ mol } Cl_2\end{aligned}$$

Because the final volume of the solution is 0.100 L, the concentration of $Cr^{3+}(aq)$ is

$$[Cr^{3+}] = \frac{0.0422 \text{ mol}}{0.100 \text{ L}} = 0.422 \text{ M}$$

Related Problems: 15, 16

Titration

One of the most important techniques in analytical chemistry is **titration**—the addition of a carefully measured volume of one solution, containing substance A in known concentration, to a second solution, containing substance B in unknown concentration. Solution A is added through a buret, an instrument that accurately measures the volume of solution transferred as a stopcock is opened and then closed. As the solutions are mixed, A and B react quantitatively. Completion of the reaction, the **end point,** is signaled by a change in some physical property, such as the color of the reacting mixture. End points can be detected in colorless reaction mixtures by adding a substance called an **indicator** that changes color at the end point. At the end point, the known number of moles of substance A that has been added is uniquely related to the unknown number of moles of substance B initially present by the balanced equation for the titration reaction. Titration enables chemists to determine the unknown amount of a substance present in a sample. The two most common applications of titrations involve acid–base neutralization reactions and oxidation–reduction (or redox) reactions. We describe both here briefly to illustrate the fundamental importance of solution stoichiometry calculations in titrations. Detailed discussion of acid–base and redox reactions, and the extent to which they go to completion, are presented in Chapter 15 and Chapter 17, respectively.

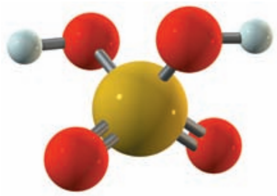
Background on Acid–Base Reactions

Table 11.1 lists the names and formulas of a number of important acids. Acids and bases have been known and characterized since ancient times. Chemical description and explanation of their properties and behavior has progressed through several stages of sophistication and generality. A broadly applicable modern treatment is presented in Chapter 15. Here, we introduce titrations using the treatment of the Swedish chemist Svante Arrhenius, who defined acids and bases by their behavior when dissolved in water.

TABLE 11.1 Names of Common Acids

Binary Acids	Oxoacids	Organic Acids
HF, hydrofluoric acid	H_2CO_3, carbonic acid	HCOOH, formic acid
HCl, hydrochloric acid	H_3PO_3, phosphorus acid	CH_3COOH, acetic acid
HCN, hydrocyanic acid[†]	H_3PO_4, phosphoric acid	C_6H_5COOH, benzoic acid
H_2S, hydrosulfuric acid	HNO_2, nitrous acid	HOOCCOOH, oxalic acid
	HNO_3, nitric acid	
	H_2SO_3, sulfurous acid	
	H_2SO_4, sulfuric acid	
	HClO, hypochlorous acid	
	$HClO_2$, chlorous acid	
	$HClO_3$, chloric acid	
	$HClO_4$, perchloric acid	

[†] Contains three elements but is named as a binary acid.



Sulfuric acid, H_2SO_4, is the industrial chemical produced on the largest scale in the world, in amounts exceeding 100 million tons per year.

In pure water, small but equal numbers of hydronium ions (H_3O^+) and hydroxide ions (OH^-) are present.[1] These arise from the partial ionization of water:

$$2\ H_2O(\ell) \longrightarrow H_3O^+(aq) + OH^-(aq)$$

Following Arrhenius, we define an **acid** as a substance that when dissolved in water increases the number of hydronium ions over the number present in pure water. Gaseous hydrogen chloride reacts with water to give hydrochloric acid:

$$H_2O(\ell) + HCl(g) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

A **base** is defined as a substance that when dissolved increases the number of hydroxide ions over the number present in pure water. Sodium hydroxide dissolves extensively in water according to the following reaction:

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$

Ammonia is another base, as shown by the products of its reaction with water:

$$NH_3(aq) + H_2O(\ell) \longrightarrow NH_4^+(aq) + OH^-(aq)$$

Hydrochloric acid, HCl, is used in the pickling of steel and other metals to remove oxide layers on the surface.

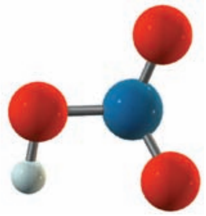
When an acidic solution is mixed with a basic solution, a **neutralization reaction** occurs:

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2\ H_2O(\ell)$$

This is the reverse of the water ionization reaction shown earlier. If the spectator ions are put back into the equation, it reads

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NaOH} \longrightarrow \underset{\text{Water}}{H_2O} + \underset{\text{Salt}}{NaCl}$$

showing that a salt can be defined as the product (other than water) of the reaction of an acid with a base. It is usually preferable to omit the spectator ions and to indicate explicitly only the reacting ions.



Nitric acid, HNO_3, is manufactured from ammonia.

Acid–Base Titration

In most acid–base reactions, there is no sharp color change at the end point. In such cases it is necessary to add a small amount of an indicator, a dye that changes color when the reaction is complete (indicators are discussed in detail in

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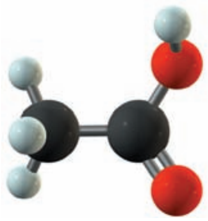
[1] As discussed in Chapter 15, a hydrogen ion in aqueous solution is closely held by a water molecule and is better represented as a hydronium ion, $H_3O^+(aq)$.



Acetic acid, CH_3COOH, is a common organic acid that is found in vinegar as a 3% to 5% solution by mass.

Section 15.3). Phenolphthalein is such an indicator, changing from colorless to pink when a solution changes from acidic to basic. The concentration of acetic acid in an aqueous solution can be determined by adding a few drops of a phenolphthalein solution and then titrating it with a solution of sodium hydroxide of accurately known concentration. At the first permanent appearance of a pink color, the stopcock of the buret is closed. At this point, the reaction

$$\text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq) \longrightarrow \text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(\ell)$$

has gone stoichiometrically to completion.

EXAMPLE 11.6

A sample of vinegar is to be analyzed for its acetic acid content. A volume of 50.0 mL is measured out and titrated with a solution of 1.306 M NaOH; 31.66 mL of that titrant is required to reach the phenolphthalein end point. Calculate the concentration of acetic acid in the vinegar (in moles per liter).

SOLUTION

The number of moles of NaOH reacting is found by multiplying the volume of NaOH solution (31.66 mL = 0.03166 L) by its concentration (1.306 M):

$$0.03166 \text{ L} \times 1.306 \text{ mol L}^{-1} = 4.135 \times 10^{-2} \text{ mol NaOH}$$

Because 1 mol of acetic acid reacts with 1 mol of $\text{OH}^-(aq)$, the number of moles of acetic acid originally present must also have been 4.135×10^{-2} mol. Its concentration was then

$$[\text{CH}_3\text{COOH}] = \frac{4.135 \times 10^{-2} \text{ mol}}{0.0500 \text{ L}} = 0.827 \text{ M}$$

Related Problems: 25, 26

11.4 Reaction Stoichiometry in Solutions: Oxidation–Reduction Titrations

Background on Oxidation–Reduction (Redox) Reactions

In **oxidation–reduction** (or **redox**) **reactions,** electrons are transferred between reacting species as they combine to form products. This exchange is described as a change in the oxidation number of the reactants: The oxidation number of the species giving up electrons increases, whereas that for the species accepting electrons decreases. Oxidation numbers are defined and methods for their calculation are presented in Section 3.10. A prototype redox reaction is that of magnesium (Mg) with oxygen (O) (Fig. 11.6). When this reaction is carried to completion, the product is magnesium oxide:

$$2\ \text{Mg}(s) + \text{O}_2(g) \longrightarrow 2\ \text{MgO}(s)$$

Magnesium is **oxidized** in this process; it *gives up* electrons as its oxidation number *increases* from 0 (in elemental Mg) to +2 (in MgO). Oxygen, which accepts these electrons, is said to be reduced; its oxidation number decreases from 0 to −2. The transfer of electrons (e^-) can be indicated with arrows:

$$2\ \underset{\downarrow}{\overset{0}{\text{Mg}}} + \underset{\uparrow}{\overset{0}{\text{O}_2}} \longrightarrow 2\ \overset{+2}{\text{Mg}}\overset{-2}{\text{O}}$$
$$2 \times 2e^- = 2 \times 2e^-$$

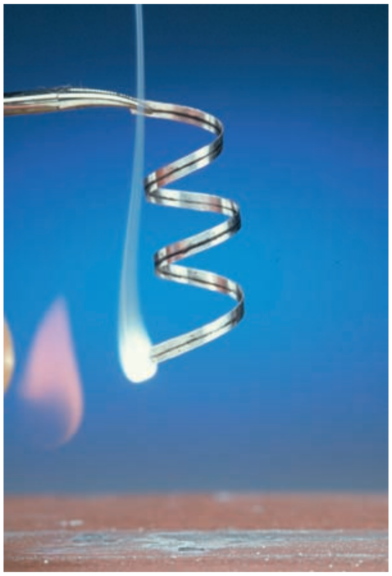


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FIGURE 11.6 Magnesium burning in air gives off an extremely bright light. This characteristic led to the incorporation of magnesium into the flash powder used in early photography. Magnesium powder is still used in fireworks for the same reason.

The arrows point away from the species being oxidized (giving up electrons) and toward the species being reduced (accepting electrons). The electron "bookkeeping" beneath the equation ensures that the same number of electrons are taken up by oxygen as are given up by magnesium:

$$\begin{aligned}&2\text{ Mg atoms} \times 2\text{ electrons per Mg atom} = \\ &\qquad 2\text{ O atoms per formula unit} \times 2\text{ electrons per O atom}\end{aligned}$$

Originally, the term *oxidation* referred only to reactions with oxygen. It now is used to describe any process in which the oxidation number of a species increases, even if oxygen is not involved in the reaction. When calcium combines with chlorine to form calcium chloride,

$$\underset{\underset{2e^-}{\downarrow}}{\overset{0}{\mathrm{Ca}}}(s) + \underset{\underset{2 \times 1e^-}{\uparrow}}{\overset{0}{\mathrm{Cl}_2}}(g) \longrightarrow \overset{+2\;-1}{\mathrm{CaCl}_2}$$

$$2e^- \;=\; 2 \times 1e^-$$

the calcium has been oxidized and the chlorine has been reduced.

Oxidation–reduction reactions are among the most important in chemistry, biochemistry, and industry. Combustion of coal, natural gas, and gasoline for heat and power are redox reactions, as are the recovery of metals such as iron and aluminum from their oxide ores and the production of chemicals such as sulfuric acid from sulfur, air, and water. The human body metabolizes sugars through redox reactions to obtain energy; the reaction products are liquid water and gaseous carbon dioxide.

EXAMPLE 11.7

Determine whether the following equations represent oxidation–reduction reactions.

(a) $SnCl_2(s) + Cl_2(g) \longrightarrow SnCl_4(\ell)$

(b) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

(c) $2\ H_2O_2(\ell) \longrightarrow 2\ H_2O(\ell) + O_2(g)$

SOLUTION

(a) Tin increases its oxidation number from +2 to +4, and the oxidation number of chlorine in Cl_2 is reduced from 0 to −1. Some other chlorine atoms are unchanged in oxidation number, but this is still a redox reaction.

(b) The oxidation state of Ca remains at +2, that of O at −2, and that of C at +4. Thus, this is not a redox reaction.

(c) The oxidation number of oxygen in H_2O_2 is −1. This changes to −2 in the product H_2O and 0 in O_2. This is a redox reaction in which the same element is both oxidized and reduced.

Related Problems: 27, 28, 29, 30

Balancing Oxidation–Reduction Equations in Aqueous Solution

Numerous redox reactions occur in aqueous solution. For example, consider the reaction between solid copper (Cu) and an aqueous solution of silver (Ag) nitrate:

$$Cu(s) + 2\ Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\ Ag(s)$$

The nitrate ions are spectators that do not take part in the reaction, so they are omitted in the net equation. Two electrons are transferred from each reacting Cu atom to a pair of silver ions. Copper (the electron donor) is oxidized, and silver ion (the electron acceptor) is reduced. This oxidation–reduction reaction occurs when a piece of copper is placed in an aqueous solution of silver nitrate or any other soluble silver salt (Fig. 11.7). Metallic silver immediately begins to plate out on the copper, the concentration of silver ion decreases, and blue $Cu^{2+}(aq)$ appears in solution and increases in concentration as time passes.

It is useful to consider this chemical equation as representing the sum of oxidation and reduction **half-reactions,** in which electrons (e^-) appear explicitly. The oxidation of copper is written as

$$\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\,e^-$$

and the reduction of silver ion as

$$\mathrm{Ag}^+(aq) + e^- \longrightarrow \mathrm{Ag}(s)$$

In the net equation, electrons must not appear explicitly. Thus, the second equation must be multiplied by 2 before being added to the first so that the electrons cancel out on both sides. As before, this gives

$$\mathrm{Cu}(s) + 2\,\mathrm{Ag}^+(aq) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\,\mathrm{Ag}(s)$$

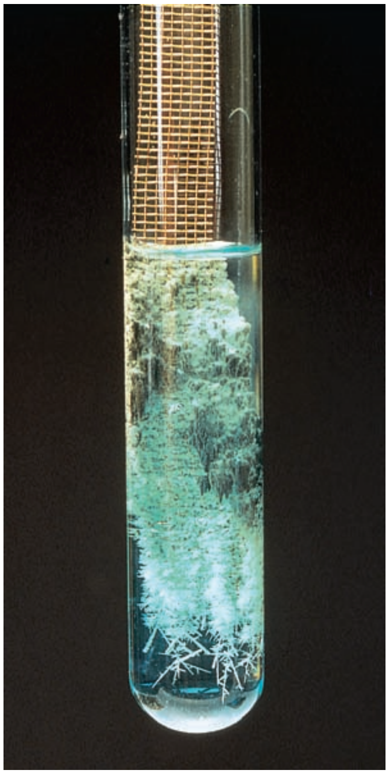
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FIGURE 11.7 When a piece of copper screen is inserted into a solution of silver nitrate, silver forms in a tree-like structure and the solution turns blue as Cu^{2+} ions form.

Many redox reactions are too difficult to balance by the simple methods of logical reasoning described in Section 2.4. Here, we outline a systematic procedure based on half-reactions and apply it to reactions that occur in acidic or basic aqueous solution. In these reactions, water and H_3O^+ (acidic solution) or OH^- (basic solution) may take part either as reactants or as products; thus, it is necessary to *complete* the corresponding equations, as well as to balance them.

As an example, let's complete and balance the chemical equation for the dissolution of copper(II) sulfide in aqueous nitric acid (Fig. 11.8):

$$\mathrm{CuS}(s) + \mathrm{NO}_3^-(aq) \longrightarrow \mathrm{Cu}^{2+}(aq) + \mathrm{SO}_4^{2-}(aq) + \mathrm{NO}(g)$$

Step 1 *Write two unbalanced half-equations, one for the species that is oxidized and its product and one for the species that is reduced and its product.*

Here, the unbalanced half-reaction involving CuS is

$$\mathrm{CuS} \longrightarrow \mathrm{Cu}^{2+} + \mathrm{SO}_4^{2-}$$

The unbalanced half-reaction involving NO_3^- is

$$\mathrm{NO}_3^- \longrightarrow \mathrm{NO}$$

Step 2 *Insert coefficients to make the numbers of atoms of all elements except oxygen and hydrogen equal on the two sides of each equation.*

In this case, copper, sulfur, and nitrogen are already balanced in the two half-equations, so this step is already completed.

Step 3 *Balance oxygen by adding H_2O to one side of each half-equation.*

$$\mathrm{CuS} + 4\,\mathrm{H_2O} \longrightarrow \mathrm{Cu}^{2+} + \mathrm{SO}_4^{2-}$$

$$\mathrm{NO}_3^- \longrightarrow \mathrm{NO} + 2\,\mathrm{H_2O}$$

Step 4 *Balance hydrogen. For an acidic solution, add H_3O^+ to the side of each half-equation that is "deficient" in hydrogen and add an equal amount of H_2O to the other side. For a basic solution, add H_2O to the side of each half-equation that is "deficient" in hydrogen and add an equal amount of OH^- to the other side.*

Note that this step does not disrupt the oxygen balance achieved in step 3. In this case (acidic solution), the result is

$$\mathrm{CuS} + 12\,\mathrm{H_2O} \longrightarrow \mathrm{Cu}^{2+} + \mathrm{SO}_4^{2-} + 8\,\mathrm{H_3O}^+$$

$$\mathrm{NO}_3^- + 4\,\mathrm{H_3O}^+ \longrightarrow \mathrm{NO} + 6\,\mathrm{H_2O}$$


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FIGURE 11.8 Copper(II) sulfide reacts with concentrated nitric acid to liberate nitrogen oxide and produce a solution of copper(II) sulfate, which displays the characteristic blue color of copper(II) ions in water.

Step 5 *Balance charge by inserting* e^- *(electrons) as a reactant or product in each half-equation.*

$$\text{CuS} + 12\ \text{H}_2\text{O} \longrightarrow \text{Cu}^{2+} + \text{SO}_4^{2-} + 8\ \text{H}_3\text{O}^+ + 8\ e^-$$

(oxidation)

$$\text{NO}_3^- + 4\ \text{H}_3\text{O}^+ + 3\ e^- \longrightarrow \text{NO} + 6\ \text{H}_2\text{O}$$

(reduction)

Step 6 *Multiply the two half-equations by numbers chosen to make the number of electrons given off by the oxidation equal the number taken up by the reduction. Then add the two half-equations, canceling electrons. If* H_3O^+*,* OH^-*, or* H_2O *appears on both sides of the final equation, cancel out the duplications.*

Here, the oxidation half-equation must be multiplied by 3 (so that 24 electrons are produced), and the reduction half-equation by 8 (so that the same 24 electrons are consumed):

$$\begin{array}{r}
3\ \text{CuS} + 36\ \text{H}_2\text{O} \longrightarrow 3\ \text{Cu}^{2+} + 3\ \text{SO}_4^{2-} + 24\ \text{H}_3\text{O}^+ + 24\ e^- \\
8\ \text{NO}_3^- + 32\ \text{H}_3\text{O}^+ + 24\ e^- \longrightarrow 8\ \text{NO} + 48\ \text{H}_2\text{O} \\
\hline
3\ \text{CuS} + 8\ \text{NO}_3^- + 8\ \text{H}_3\text{O}^+ \longrightarrow 3\ \text{Cu}^{2+} + 3\ \text{SO}_4^{2-} + 8\ \text{NO} + 12\ \text{H}_2\text{O}
\end{array}$$

This procedure balances equations that are too difficult to balance by inspection. For basic solutions, remember to add H_2O and OH^-, rather than H_3O^+ and H_2O, at step 4.

EXAMPLE 11.8

Balance the following equation, which represents a reaction that occurs in basic aqueous solution:

$$\text{Ag}(s) + \text{HS}^-(aq) + \text{CrO}_4^{2-}(aq) \longrightarrow \text{Ag}_2\text{S}(s) + \text{Cr(OH)}_3(s)$$

SOLUTION

Step 1

$$\text{Ag} + \text{HS}^- \longrightarrow \text{Ag}_2\text{S}$$

$$\text{CrO}_4^{2-} \longrightarrow \text{Cr(OH)}_3$$

Step 2

$$2\ \text{Ag} + \text{HS}^- \longrightarrow \text{Ag}_2\text{S}$$

The other half-reaction is unchanged.

Step 3 H_2O is now added to the second half-reaction to balance oxygen:

$$\text{CrO}_4^{2-} \longrightarrow \text{Cr(OH)}_3 + \text{H}_2\text{O}$$

Step 4 The right side of the silver half-reaction is deficient by 1 H. Add 1 H_2O to the right and 1 OH^- to the left:

$$2\ \text{Ag} + \text{HS}^- + \text{OH}^- \longrightarrow \text{Ag}_2\text{S} + \text{H}_2\text{O}$$

In the chromium half-reaction, the left side is deficient by 5 H atoms, so 5 H_2O is added to that side and 5 OH^- to the right side:

$$\text{CrO}_4^{2-} + 4\ \text{H}_2\text{O} \longrightarrow \text{Cr(OH)}_3 + 5\ \text{OH}^-$$

(Notice that the H_2O on the right canceled out one of the five on the left, leaving four.)

Step 5 Electrons are added to the right side of the silver half-reaction and to the left side of the chromium half-reaction to balance charge:

$$2\ \text{Ag} + \text{Hs}^- + \text{OH}^- \longrightarrow \text{Ag}_2\text{S} + \text{H}_2\text{O} + 2\ e^-$$

(oxidation)

$$\text{CrO}_4^{2-} + 4\ \text{H}_2\text{O} + 3\ e^- \longrightarrow \text{Cr(OH)}_3 + 5\ \text{OH}^-$$

(reduction)

Step 6 The gain and loss of electrons are equalized. The first equation is multiplied by 3 so that it consumes six electrons, and the second is multiplied by 2 so that it produces six electrons.

$$\underset{\text{(oxidation)}}{6\ Ag + 3\ HS^- + 3\ OH^-} \longrightarrow 3\ Ag_2S + 3\ H_2O + 6\ e^-$$

$$\underset{\text{(reduction)}}{2\ CrO_4^{2-} + 8\ H_2O + 6\ e^-} \longrightarrow 2\ Cr(OH)_3 + 10\ OH^-$$

$$6\ Ag + 3\ HS^- + 2\ CrO_4^{2-} + 5\ H_2O \longrightarrow 3\ Ag_2S + 2\ Cr(OH)_3 + 7\ OH^-$$

Related Problems: 31, 32, 33, 34

EXAMPLE 11.9

Balance the following equation for the reaction of arsenic(III) sulfide with aqueous chloric acid:

$$As_2S_3(s) + ClO_3^-(aq) \longrightarrow H_3AsO_4(aq) + SO_4^{2-}(aq) + Cl^-(aq)$$

SOLUTION

Step 1

$$As_2S_3 \longrightarrow H_3AsO_4 + SO_4^{2-}$$

$$ClO_3^- \longrightarrow Cl^-$$

Step 2

$$As_2S_3 \longrightarrow 2\ H_3AsO_4 + 3\ SO_4^{2-}$$

Step 3

$$As_2S_3 + 20\ H_2O \longrightarrow 2\ H_3AsO_4 + 3\ SO_4^{2-}$$

$$ClO_3^- \longrightarrow Cl^- + 3\ H_2O$$

Step 4 The chloric acid makes this an acidic solution, so H_3O^+ and H_2O are used:

Step 5

$$As_2S_3 + 54\ H_2O \longrightarrow 2\ H_3AsO_4 + 3\ SO_4^{2-} + 34\ H_3O^+$$

$$ClO_3^- + 6\ H_3O^+ \longrightarrow Cl^- + 9\ H_2O$$

$$As_2S_3 + 54\ H_2O \longrightarrow 2\ H_3AsO_4 + 3\ SO_4^{2-} + 34\ H_3O^+ + 28\ e^-$$

$$ClO_3^- + 6\ H_3O^+ + 6\ e^- \longrightarrow Cl^- + 9\ H_2O$$

Step 6 We must find the least common multiple of 28 and 6. This is 84; therefore, we need to multiply the first equation by 84/28 = 3 and the second equation by 84/6 = 14:

$$3\ As_2S_3 + 162\ H_2O \longrightarrow 6\ H_3AsO_4 + 9\ SO_4^{2-} + 102\ H_3O^+ + 84\ e^-$$

$$14\ ClO_3^- + 84\ H_3O^+ + 84\ e^- \longrightarrow 14\ Cl^- + 126\ H_2O$$

$$3\ As_2S_3 + 14\ ClO_3^- + 36\ H_2O \longrightarrow 6\ H_3AsO_4 + 9\ SO_4^{2-} + 14\ Cl^- + 18\ H_3O^+$$

Disproportionation

An important type of redox reaction, **disproportionation,** occurs when a single substance is both oxidized and reduced. Example 11.7, part (c), provided such a reaction:

$$2\ H_2\overset{-1}{O_2}(\ell) \longrightarrow 2\ H_2\overset{-2}{O}(\ell) + \overset{0}{O_2}(g)$$

The oxygen in hydrogen peroxide (H_2O_2) is in an intermediate oxidation state of −1; some of it is oxidized to O_2 and some is reduced to H_2O. The balancing of equations for disproportionation reactions is described in the following example.

EXAMPLE 11.10

Balance the following equation for the reaction that occurs when chlorine is dissolved in basic solution:

$$Cl_2(g) \longrightarrow ClO_3^-(aq) + Cl^-(aq)$$

SOLUTION

Step 1 We solve this by writing the Cl_2 on the left sides of two half-equations:

$$Cl_2 \longrightarrow ClO_3^-$$

$$Cl_2 \longrightarrow Cl^-$$

Step 2

$$Cl_2 \longrightarrow 2\ ClO_3^-$$

$$Cl_2 \longrightarrow 2\ Cl^-$$

Step 3 The first half-equation becomes

$$Cl_2 + 6\ H_2O \longrightarrow 2\ ClO_3^-$$

Step 4 Now the first half-equation becomes

$$Cl_2 + 12\ OH^- \longrightarrow 2\ ClO_3^- + 6\ H_2O$$

Step 5

$$Cl_2 + 12\ OH^- \longrightarrow 2ClO_3^- + 6\ H_2O + 10\ e^- \quad \text{(oxidation)}$$

$$Cl_2 + 2\ e^- \longrightarrow 2\ Cl^- \quad \text{(reduction)}$$

Step 6 Multiply the second equation by 5 and add:

$$\begin{array}{l} Cl_2 + 12\ OH^- \longrightarrow 2\ ClO_3^- + 6\ H_2O + 10\ e^- \\ \underline{5\ Cl_2 + 10\ e^- \longrightarrow 10\ Cl^- \qquad\qquad\qquad\quad} \\ 6\ Cl_2 + 12\ OH^- \longrightarrow 2\ ClO_3^- + 10\ Cl^- + 6\ H_2O \end{array}$$

Dividing this equation by 2 gives

$$3\ Cl_2 + 6\ OH^- \longrightarrow ClO_3^- + 5\ Cl^- + 3\ H_2O$$

Related Problems: 37, 38

Redox Titration

Redox titrations are illustrated by the reaction in which potassium permanganate oxidizes Fe^{2+} in acidic solution and the manganese (Mn) is reduced:

$$MnO_4^-(aq) + 5\ Fe^{2+}(aq) + 8\ H_3O^+(aq) \longrightarrow Mn^{2+}(aq) + 5\ Fe^{3+}(aq) + 12\ H_2O(\ell)$$

Redox titrations have the advantage that many involve intensely colored species that change color dramatically at the end point. For example, MnO_4^- is deep purple, whereas Mn^{2+} is colorless. Thus, when MnO_4^- has been added to Fe^{2+} in slight excess, the color of the solution changes permanently to purple.

The titration is begun by opening the stopcock of the buret and letting a small volume of permanganate solution run into the flask that contains the Fe^{2+} solution. A dash of purple colors the solution (Fig. 11.9a) but rapidly disappears as the permanganate ion reacts with Fe^{2+} to give the nearly colorless Mn^{2+} and Fe^{3+} products. The addition of incremental volumes of permanganate solution is continued until the Fe^{2+} is almost completely converted to Fe^{3+}. At this stage, the addition of just one drop of $KMnO_4$ imparts a pale purple color to the reaction mixture (see Fig. 11.9b) and signals the completion of the reaction. The volume of the titrant $KMnO_4$ solution is calculated by subtracting the initial reading of the solution meniscus in the buret from the final volume reading.

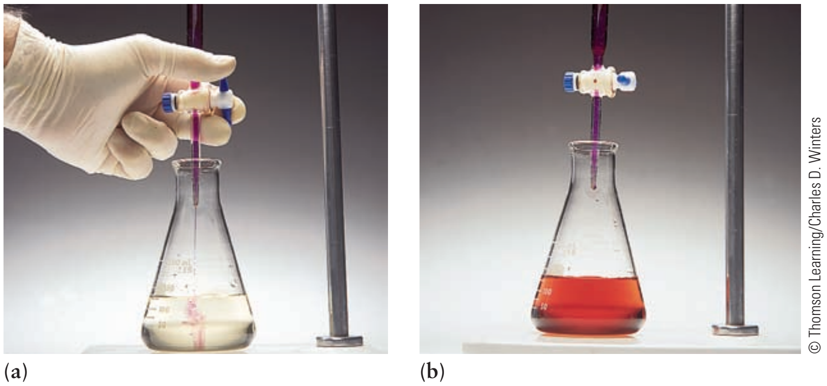
(a) (b)

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FIGURE 11.9 (a) Addition of a small amount of potassium permanganate from a buret gives a dash of purple color to the Fe^{2+} solution, which disappears quickly as the permanganate ion reacts to give Fe^{3+} and Mn^{2+}. (b) When all the Fe^{2+} ions have been consumed, additional drops of permanganate solution give a pale purple color to the solution.

Suppose that the permanganate solution has a concentration of 0.09625 M, and 26.34 mL (0.02634 L) of it is added to reach the end point. The number of moles of Fe^{2+} in the original solution is calculated in two steps:

$$\text{Amount of } MnO_4^- \text{ reacting} = 0.02634 \text{ L} \times 0.09625 \text{ mol L}^{-1}$$
$$= 2.535 \times 10^{-3} \text{ mol } MnO_4^-$$

From the balanced chemical equation, each mole of MnO_4^- used causes the oxidation of 5 mol of Fe^{2+}, so

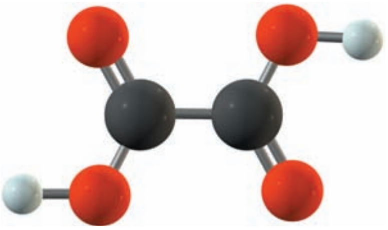
$$\text{Amount of } Fe^{2+} \text{ reacting} = 2.535 \times 10^{-3} \text{ mol } MnO_4^- \times \left(\frac{5 \text{ mol } Fe^{2+}}{1 \text{ mol } MnO_4^-}\right)$$
$$= 1.268 \times 10^{-2} \text{ mol } Fe^{2+}$$

These direct titrations form the basis of more complicated analytical procedures. Many analytical procedures are indirect and involve additional preliminary reactions of the sample before the titration can be carried out. For example, a soluble calcium salt will not take part in a redox reaction with potassium permanganate. But adding ammonium oxalate to the solution containing Ca^{2+} causes the quantitative precipitation of calcium oxalate:

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) \longrightarrow CaC_2O_4(s)$$

After the precipitate is filtered and washed, it is dissolved in sulfuric acid to form oxalic acid:

$$CaC_2O_4(s) + 2\ H_3O^+(aq) \longrightarrow Ca^{2+}(aq) + H_2C_2O_4(aq) + 2\ H_2O$$



Oxalic acid, $H_2C_2O_4$, is an acid that can give up two H ions in aqueous solution to form the oxalate ion, $C_2O_4^{2-}$.

Finally, the oxalic acid is titrated with permanganate solution of accurately known concentration, based on the redox reaction

$$2\ MnO_4^-(aq) + 5\ H_2C_2O_4(aq) + 6\ H_3O^+(aq) \longrightarrow$$
$$2\ Mn^{2+}(aq) + 10\ CO_2(g) + 14\ H_2O(\ell)$$

In this way, the quantity of calcium can be determined indirectly by reactions that involve precipitation, acid–base, and redox steps.

11.5 Phase Equilibrium in Solutions: Nonvolatile Solutes

We turn now from the chemical reactions of solutions to such physical properties as their vapor pressures and phase diagrams. Consider first a solution made by dissolving a nonvolatile solute in a solvent. By "nonvolatile" we mean that the vapor pressure of the solute above the solution is negligible. An example is a solution of sucrose (cane sugar) in water, in which the vapor pressure of sucrose above the solution is zero. We study the case of a volatile solute in Section 11.6.

The *solvent* vapor pressure is not zero and changes with the composition of the solution at a fixed temperature. If the mole fraction of solvent (X_1) is 1, then the vapor pressure is P_1°, the vapor pressure of pure solvent at the temperature of the experiment. When X_1 approaches 0 (giving pure solute), the vapor pressure P_1 of the solvent must go to 0 also, because solvent is no longer present. As the mole fraction X_1 changes from 1 to 0, P_1 drops from P_1° to 0. What is the shape of the curve?

The French chemist François-Marie Raoult found that for some solutions a plot of solvent vapor pressure against solvent mole fraction can be fitted closely by a straight line (Fig. 11.10). Solutions that conform to this straight-line relationship obey the following simple equation:

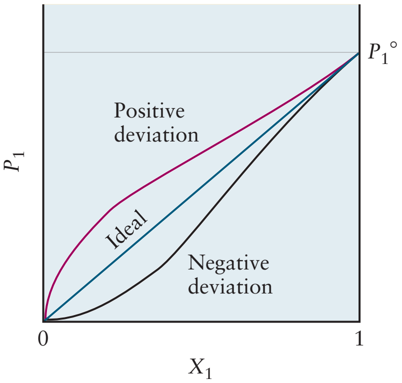


FIGURE 11.10 In an ideal solution, a graph of solvent vapor pressure P_1 versus mole fraction of solvent X_1 is a straight line. Nonideal solutions behave differently; examples of positive and negative deviations from the ideal solution are shown. The vapor pressure of pure solvent is P_1°.

$$P_1 = X_1 P_1^\circ \qquad [11.5]$$

which is known as **Raoult's law.** Such solutions are called **ideal solutions.** Other solutions deviate from straight-line behavior and are called **nonideal solutions.** They may show positive deviations (with vapor pressures higher than those predicted by Raoult's law) or negative deviations (with lower vapor pressures). On a molecular level, negative deviations arise when the solute attracts solvent molecules especially strongly, reducing their tendency to escape into the vapor phase. Positive deviations arise in the opposite case, when solvent and solute molecules are not strongly attracted to each other. Even nonideal solutions with nondissociating solutes approach Raoult's law as X_1 approaches 1, just as all real gases obey the ideal gas law at sufficiently low densities.

Raoult's law forms the basis for four properties of dilute solutions, which are called **colligative properties** (derived from Latin *colligare*, meaning "to collect together") because they depend on the collective effect of the *number* of dissolved particles rather than on the *nature* of the particular particles involved. These four properties are:

1. The lowering of the vapor pressure of a solution relative to pure solvent
2. The elevation of the boiling point
3. The depression of the freezing point
4. The phenomenon of osmotic pressure

Vapor-Pressure Lowering

Because $X_1 = 1 - X_2$ for a two-component solution, Raoult's law can be rewritten as

$$\Delta P_1 = P_1 - P_1^\circ = X_1 P_1^\circ - P_1^\circ = -X_2 P_1^\circ \qquad [11.6]$$

so that the *change* in vapor pressure of the solvent is proportional to the mole fraction of solute. The negative sign implies **vapor-pressure lowering;** the vapor pressure is always less above a dilute solution than it is above the pure solvent.

EXAMPLE 11.11

At 25°C, the vapor pressure of pure benzene is $P_1^\circ = 0.1252$ atm. Suppose 6.40 g of naphthalene, $C_{10}H_8$ (molar mass 128.17 g mol^{-1}), is dissolved in 78.0 g of benzene (molar mass 78.0 g mol^{-1}). Calculate the vapor pressure of benzene over the solution, assuming ideal behavior.

SOLUTION

The number of moles of solvent, n_1, is 1.00 mol in this case (because 78.0 g = 1.00 mol benzene has been used). The number of moles of solute is $n_2 = 6.40 \text{ g}/128.17 \text{ g mol}^{-1} = 0.0499 \text{ mol } C_{10}H_8$; thus, the mole fraction X_1 is

$$X_1 = \frac{n_1}{n_1 + n_2} = \frac{1.00 \text{ mol}}{1.00 + 0.0499 \text{ mol}} = 0.9525$$

From Raoult's law, the vapor pressure of benzene above the solution is

$$P_1 = X_1 P_1^\circ = 0.9525 \times 0.1252 \text{ atm} = 0.119 \text{ atm}$$

Related Problems: 41, 42

Boiling-Point Elevation

The normal boiling point of a pure liquid T_b or a solution T_b' is the temperature at which the vapor pressure reaches 1 atm. Because a dissolved solute reduces the vapor pressure, the temperature of the solution must be increased to make it boil. That is, the boiling point of a solution is higher than that of the pure solvent. This phenomenon, referred to as **boiling-point elevation,** provides a method for determining molar masses.

The vapor-pressure curve of a dilute solution lies slightly below that for the pure solvent. In Figure 11.11, ΔP_1 is the decrease of vapor pressure at T_b and ΔT_b is the change in temperature necessary to hold the vapor pressure at 1 atm (that is, $\Delta T_b = T_b' - T_b$ is the increase in boiling point caused by addition of solute to the pure solvent). For small concentrations of nondissociating solutes, the two curves are parallel, so

$$-\frac{\Delta P_1}{\Delta T_b} = \text{slope of curve} = S$$

$$\Delta T_b = -\frac{\Delta P_1}{S} = \frac{X_2 P_1^\circ}{S}$$

$$= \frac{1}{S}\left(\frac{n_2}{n_1 + n_2}\right) \qquad \text{(from Raoult's law, with } P_1^\circ = 1 \text{ atm)}$$

The constant S is a property of the pure solvent only, because it is the slope of the vapor pressure curve $\Delta P_1/\Delta T_b$ near 1 atm pressure. That is, S is independent of the solute species involved.

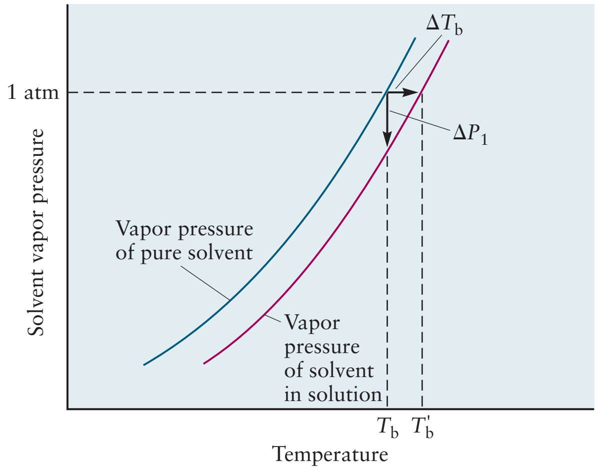


FIGURE 11.11 The vapor pressure of the solvent above a dilute solution is lower than that of the pure solvent at all temperatures. As a result, for the solution to boil (that is, for the vapor pressure to reach 1 atm), a higher temperature is required for the solution than for the pure solvent. This amounts to an elevation of the boiling point.

TABLE 11.2 Boiling-Point Elevation and Freezing-Point Depression Constants

Solvent	Formula	T_b (°C)	K_b (K kg mol^{-1})	T_f (°C)	K_f (K kg mol^{-1})
Acetic acid	CH_3COOH	118.1	3.07	17	3.9
Benzene	C_6H_6	80.1	2.53	5.5	4.9
Carbon tetrachloride	CCl_4	76.7	5.03	−22.9	32
Diethyl ether	$C_4H_{10}O$	34.7	2.02	−116.2	1.8
Ethanol	C_2H_5OH	78.4	1.22	−114.7	1.9
Naphthalene	$C_{10}H_8$	—	—	80.5	6.8
Water	H_2O	100.0	0.512	0.0	1.86

For very dilute solutions, $n_1 \gg n_2$; this may be simplified as follows:

$$\Delta T_b = \frac{1}{S}\frac{n_2}{n_1} = \frac{1}{S}\left(\frac{m_2/\mathcal{M}_2}{m_1/\mathcal{M}_1}\right)$$

where m_1 and m_2 are the masses of solvent and solute (in grams) and $\mathcal{M}_1$ and $\mathcal{M}_2$ are their molar masses in grams per mole. Because $\mathcal{M}_1$, like S, is a property of the solvent only, it is convenient to combine the two and define a new constant K_b through

$$K_b = \frac{\mathcal{M}_1}{(1000 \text{ g kg}^{-1})S}$$

Then

$$\Delta T_b = K_b\left(\frac{m_2/\mathcal{M}_2}{m_1/(1000 \text{ g kg}^{-1})}\right)$$

Because m_1 is measured in grams, $m_1/(1000 \text{ g kg}^{-1})$ is the number of kilograms of solvent. Also, $m_2/\mathcal{M}_2$ is the number of moles of solute. The expression in parentheses is, therefore, the molality (m) of the solution.

$$\boxed{\Delta T_b = K_b m} \qquad [11.7]$$

For a given solvent, K_b is obtained by measuring the boiling-point elevations for dilute solutions of known molality (that is, containing a known amount of solute with known molar mass). Table 11.2 gives values of K_b for a number of solvents. Once K_b has been found, it can be used either to predict boiling-point elevations for solutes of known molar mass or to determine molar masses from measured boiling-point elevations, as illustrated in part (b) of the following example.

EXAMPLE 11.12

(a) When 5.50 g of biphenyl ($C_{12}H_{10}$) is dissolved in 100.0 g of benzene, the boiling point increases by 0.903°C. Calculate K_b for benzene.

(b) When 6.30 g of an unknown hydrocarbon is dissolved in 150.0 g of benzene, the boiling point of the solution increases by 0.597°C. What is the molar mass of the unknown substance?

SOLUTION

(a) Because the molar mass of biphenyl is 154.2 g mol^{-1}, 5.50 g contains 5.50 g/154.2 g mol^{-1} = 0.0357 mol. The molality, m, is

$$m = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{0.0357 \text{ mol}}{0.1000 \text{ kg}} = 0.357 \text{ mol kg}^{-1}$$

$$K_b = \frac{\Delta T_b}{m} = \frac{0.903 \text{ K}}{0.357 \text{ mol kg}^{-1}} = 2.53 \text{ K kg mol}^{-1} \text{ for benzene}$$

(b) Solving $\Delta T_b = K_b m$ for m gives

$$m = \frac{\Delta T_b}{K_b} = \frac{0.597 \text{ K}}{2.53 \text{ K kg mol}^{-1}} = 0.236 \text{ mol kg}^{-1}$$

The number of moles of solute is the product of the molality of the solution and the mass of the solvent, m_1:

$$n_2 = (0.236 \text{ mol kg}^{-1}) \times (0.1500 \text{ kg}) = 0.0354 \text{ mol}$$

Finally, the molar mass of the solute is its mass divided by its number of moles:

$$\text{molar mass of solute} = \mathcal{M}_2 = \frac{m_2}{n_2} = \frac{6.30 \text{ g}}{0.0354 \text{ mol}} = 178 \text{ g mol}^{-1}$$

The unknown hydrocarbon might be anthracene ($C_{14}H_{10}$), which has a molar mass of 178.24 g mol^{-1}.

Related Problems: 43, 44, 45, 46

So far, only *nondissociating* solutes have been considered. Colligative properties depend on the total number of moles per liter of dissolved species present. If a solute dissociates (as sodium chloride dissolves to furnish Na^+ and Cl^- ions in aqueous solution), then the molality, m, to be used is the *total* molality. One mole of NaCl dissolves to give 2 mol of ions; thus, the total molality and the boiling-point elevation are twice as large as they would be if NaCl molecules were present in solution. One mole of $Ca(NO_3)_2$ dissolves to give 3 mol of ions (1 mol of Ca^{2+} and 2 mol of NO_3^-), giving 3 times the boiling-point elevation. The corresponding vapor-pressure lowering is greater as well. Ions behave differently than neutral molecules in solution, however, and nonideal behavior appears at lower concentrations in solutions that contain ions.

EXAMPLE 11.13

Lanthanum(III) chloride ($LaCl_3$) is a salt that completely dissociates into ions in dilute aqueous solution,

$$LaCl_3(s) \longrightarrow La^{3+}(aq) + 3\, Cl^-(aq)$$

yielding 4 mol of ions per mole of $LaCl_3$. Suppose 0.2453 g of $LaCl_3$ is dissolved in 10.00 g of H_2O. What is the boiling point of the solution at atmospheric pressure, assuming ideal solution behavior?

SOLUTION

The molar mass of $LaCl_3$ is 245.3 g mol^{-1}.

$$\text{moles of LaCl}_3 = \frac{0.2453 \text{ g}}{245.3 \text{ g mol}^{-1}}$$

$$= 1.000 \times 10^{-3} \text{ mol}$$

$$\text{total molality} = m = \frac{(4)(1.000 \times 10^{-3}) \text{ mol of ions}}{0.0100 \text{ kg solvent}}$$

$$= 0.400 \text{ mol kg}^{-1}$$

This is inserted into the equation for the boiling-point elevation:

$$\Delta T_b = K_b m = (0.512 \text{ K kg mol}^{-1})(0.400 \text{ mol kg}^{-1}) = 0.205 \text{ K}$$

$$T_b = 100.205°\text{C}$$

The actual boiling point is slightly lower than this because the solution is nonideal.

Freezing-Point Depression

The phenomenon of **freezing-point depression** is analogous to that of boiling-point elevation. Here, we consider only cases in which the first solid that crystallizes from solution is the pure solvent. If solute crystallizes out with solvent, the situation is more complicated.

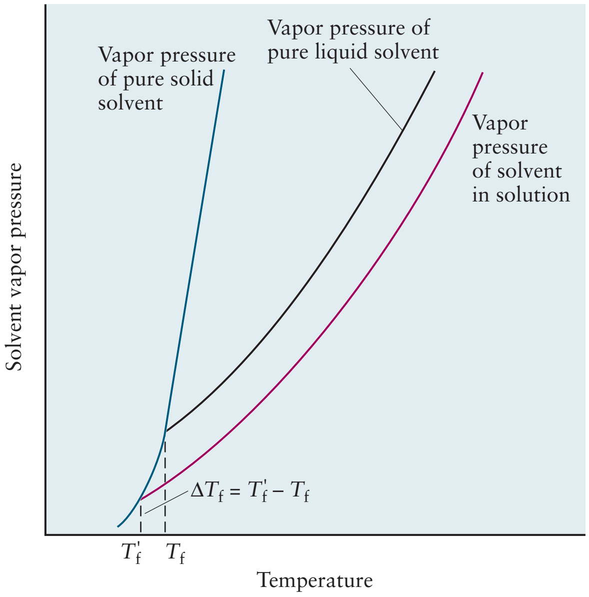
Pure solid solvent coexists at equilibrium with its characteristic vapor pressure, determined by the temperature (Section 10.4). Solvent in solution likewise coexists with a certain vapor pressure of solvent. If solid solvent and the solvent in solution are to coexist, they must have the *same* vapor pressure. This means that the freezing temperature of a solution can be identified as the temperature at which the vapor-pressure curve of the pure solid solvent intersects that of the solution (Fig. 11.12). As solute is added to the solution, the vapor pressure of the solvent falls and the freezing point, the temperature at which the first crystals of pure solvent begin to appear, drops. The difference $\Delta T_f = T_f' - T_f$ is therefore negative, and a freezing-point depression is observed.

The change in temperature, ΔT_f, is once again proportional to the change in vapor pressure, ΔP_1. For sufficiently small concentrations of solute, the freezing-point depression is related to the total molality, m (by analogy with the case of boiling-point elevation), through

$$\Delta T_f = T_f' - T_f = -K_f m \qquad [11.8]$$

where K_f is a positive constant that depends only on the properties of the solvent (see Table 11.2). Freezing-point depression is responsible for the fact that seawater, containing dissolved salts, has a slightly lower freezing point than fresh water. Concentrated salt solutions have still lower freezing points. Salt spread on an icy road reduces the freezing point of the ice, so the ice melts.

FIGURE 11.12 The vapor pressure of solvent above a dilute solution, compared with that above pure liquid and solid solvent. The depression of the freezing point from T_f to T_f' is shown.



Measurements of the drop in the freezing point, like those of elevation of the boiling point, can be used to determine molar masses of unknown substances. If a substance dissociates in solution, the *total* molality of all species present (ionic or neutral) must be used in the calculation.

EXAMPLE 11.14

The number of moles of the major dissolved species in a 1.000-L sample of seawater are as follows. Estimate the freezing point of the seawater, assuming $K_f = 1.86$ K kg mol^{-1} for water.

Na^+	0.458 mol	Cl^-	0.533 mol
Mg^{2+}	0.052 mol	SO_4^{2-}	0.028 mol
Ca^{2+}	0.010 mol	HCO_3^-	0.002 mol
K^+	0.010 mol	Br^-	0.001 mol
Neutral species	0.001 mol		

SOLUTION

Because water has a density of 1.00 g cm^{-3}, 1.00 L of water weighs 1.00 kg. For dilute *aqueous* solutions, the number of moles per kilogram of solvent (the molality, m) is therefore approximately equal to the number of moles per liter. The total molality, obtained by adding the individual species molalities just given, is $m = 1.095$ mol kg^{-1}. Then

$$\Delta T = -K_f m = -(1.86 \text{ K kg mol}^{-1})(1.095 \text{ mol kg}^{-1}) = -2.04 \text{ K}$$

The seawater should freeze at approximately −2°C. Nonideal solution effects make the actual freezing point slightly higher than this.

Related Problems: 47, 48

Both freezing-point depression and boiling-point elevation can be used to determine whether a species of known molar mass dissociates in solution (Fig. 11.13), as the following example shows.

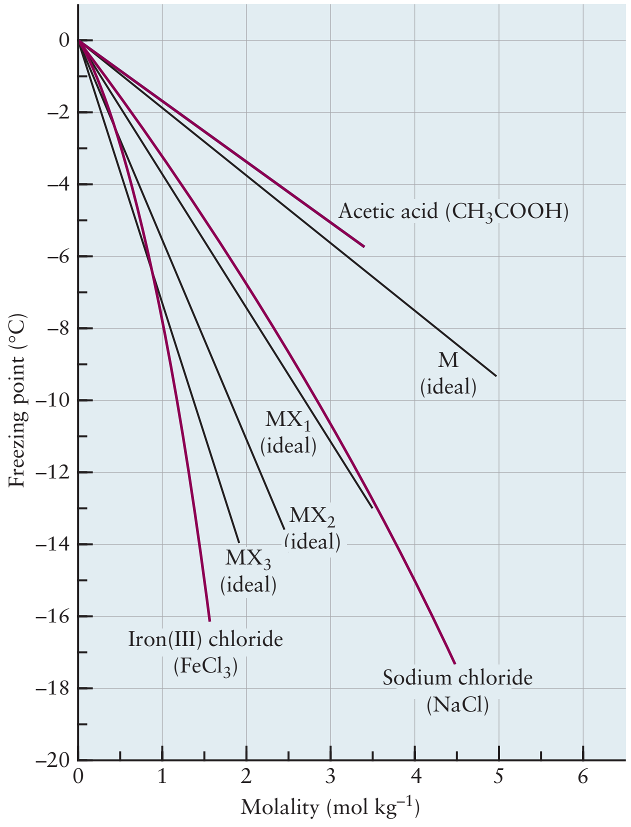


FIGURE 11.13 The heavy colored lines give the observed depression of the freezing point of water by acetic acid, NaCl, and $FeCl_3$ as the molality of the solutions increases. Straight black lines sketch the predicted ideal behavior for one through four moles of particles per mole in solution. The experimental curve for NaCl (which gives *two* moles of dissolved particles) stays close to the ideal straight line for MX; the experimental curve for $FeCl_3$ (which gives *four* moles of dissolved particles) stays fairly close to the ideal straight line for MX_3. The pattern suggests that acetic acid dissolves to give one mole of particles per mole of solute. As the molalities of the solutions increase, the observed freezing-point depressions deviate in varying ways from the straight lines.

EXAMPLE 11.15

When 0.494 g of $K_3Fe(CN)_6$ is dissolved in 100.0 g of water, the freezing point is found to be −0.093°C. How many ions are present for each formula unit of $K_3Fe(CN)_6$ dissolved?

SOLUTION

The total molality of all species in solution is

$$m = \frac{-\Delta T_f}{K_f} = \frac{0.093\text{ K}}{1.86\text{ K kg mol}^{-1}} = 0.050\text{ mol kg}^{-1}$$

Because the molar mass of $K_3Fe(CN)_6$ is 329.25 g mol^{-1}, the total molality if *no* dissociation had taken place would be

$$\frac{\left(\dfrac{0.494\text{ g}}{329.25\text{ g mol}^{-1}}\right)}{0.100\text{ kg}} = 0.0150\text{ mol kg}^{-1}$$

This is between one fourth and one third of the measured total molality in solution, so each $K_3Fe(CN)_6$ must dissociate into three to four ions. In fact, the dissociation that occurs is

$$K_3Fe(CN)_6(s) \longrightarrow 3\,K^+(aq) + [Fe(CN)_6]^{3-}(aq)$$

Deviations from ideal solution behavior have reduced the effective total molality from 0.060 to 0.050 mol kg^{-1}.

Related Problems: 51, 52

Osmotic Pressure

The fourth colligative property is particularly important in cellular biology because it plays a vital role in the transport of molecules across cell membranes. Such membranes are **semipermeable,** allowing small molecules such as water to pass through but blocking the passage of large molecules such as proteins and carbohydrates. A semipermeable membrane (for example, common cellophane) can be used to separate small solvent molecules from large solute molecules.

Suppose a solution is contained in an inverted tube, the lower end of which is covered by a semipermeable membrane. This solution has a solute concentration of *c* moles per liter. When the end of the tube is inserted in a beaker of pure solvent (Fig. 11.14), solvent flows from the beaker into the tube. The volume of the solution increases, and the solvent rises in the tube until, at equilibrium, it reaches a height, *h,* above the solvent in the beaker. The pressure on the solution side of

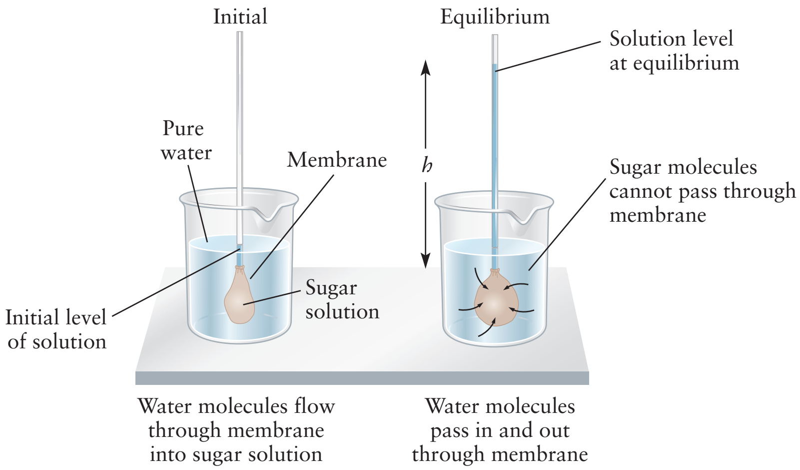
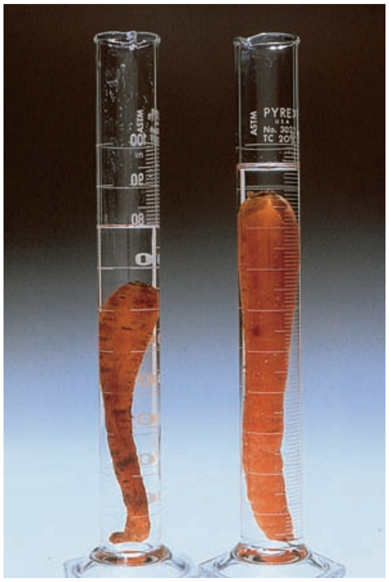


FIGURE 11.14 In this device to measure osmotic pressure, the semipermeable membrane allows solvent, but not solute, molecules to pass through. This results in a net flow of solvent into the tube until equilibrium is achieved, with the level of solution at a height, *h,* above the solvent in the beaker. Once this happens, the solvent molecules pass through the membrane at the same rate in both directions.



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When a carrot is immersed in saltwater (left), water flows out into the solution, causing the carrot to shrink. The osmotic pressure outside the cells of the vegetable is greater than that inside. A carrot left in pure water (right) does not shrivel.

the membrane is greater than the atmospheric pressure on the surface of the pure solvent by an amount given by the **osmotic pressure,** π:

$$\pi = \rho g h \qquad [11.9]$$

where ρ is the density of the solution (1.00 g cm^{-3} for a dilute aqueous solution) and g is the acceleration due to gravity (9.807 m s^{-2}).

For example, a height, h, of 0.17 m corresponds to an osmotic pressure for a dilute aqueous solution of

$$\pi = [(1.00 \text{ g cm}^{-3})(10^{-3} \text{ kg g}^{-1})(10^{6} \text{ cm}^{3} \text{ m}^{-3})](9.807 \text{ m s}^{-2})(0.17 \text{ m})$$
$$= 1.7 \times 10^{3} \text{ kg m}^{-1} \text{ s}^{-2} = 1.7 \times 10^{3} \text{ Pa}$$
$$\pi(\text{atm}) = \frac{1.7 \times 10^{3} \text{ Pa}}{1.013 \times 10^{5} \text{ Pa atm}^{-1}} = 0.016 \text{ atm}$$

This example illustrates how accurately very small osmotic pressures can be measured.

In 1887, Jacobus van't Hoff discovered an important relation among osmotic pressure, π, concentration, c, and absolute temperature, T:

$$\pi = cRT \qquad [11.10]$$

R is the gas constant, equal to 0.08206 L atm mol^{-1} K^{-1} if π is expressed in atmospheres and c in moles per liter. Because $c = n/V$, where n is the number of moles of solute and V is the volume of the solution, van't Hoff's equation can be rewritten as

$$\pi V = nRT$$

which bears a striking similarity to the ideal gas law. With this relation, the molar mass of a dissolved substance can be determined from the osmotic pressure of its solution.

EXAMPLE 11.16

A chemist dissolves 2.00 g of a protein in 0.100 L water. The osmotic pressure is 0.021 atm at 25°C. What is the approximate molar mass of the protein?

SOLUTION

The concentration in moles per liter is

$$c = \frac{\pi}{RT} = \frac{0.021 \text{ atm}}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})}$$
$$= 8.6 \times 10^{-4} \text{ mol L}^{-1}$$

Now 2.00 g dissolved in 0.100 L gives the same concentration as 20.0 g in 1.00 L. Therefore, 8.6×10^{-4} mol of protein must weigh 20.0 g, and the molar mass is

$$\mathcal{M} = \frac{20.0 \text{ g}}{8.6 \times 10^{-4} \text{ mol}} = 23{,}000 \text{ g mol}^{-1}$$

Related Problems: 53, 54

Osmotic pressure is particularly useful for measuring molar masses of large molecules such as proteins, whose solubilities may be low. In the case given in Example 11.16, the height difference h is 22 cm, an easily measured quantity. By contrast, the other three colligative properties in this example would show small effects:

$$\text{Vapor-pressure lowering} = 4.8 \times 10^{-7}\text{ atm}$$

$$\text{Boiling-point elevation} = 0.00044\text{ K}$$

$$\text{Freezing-point depression} = 0.0016\text{ K}$$

All these changes are too small for accurate measurement. As with the other techniques, the *total* number of moles of solute species determines the osmotic pressure if dissociation occurs.

Osmosis has other important uses. In some parts of the world, potable water is a precious commodity. It can be obtained much more economically by desalinizing brackish waters, through a process called **reverse osmosis,** than by distillation. When an ionic solution in contact with a semipermeable membrane has a pressure applied to it that exceeds its osmotic pressure, water of quite high purity passes through. Reverse osmosis is also used to control water pollution.

11.6 Phase Equilibrium in Solutions: Volatile Solutes

The preceding section described the properties of solutions of nonvolatile solutes in liquid solvents. The concept of an ideal solution can be extended to mixtures of two or more components, each of which is volatile. In this case, an ideal solution is one in which the vapor pressure of *each* species present is proportional to its mole fraction in solution over the whole range of mole fraction:

$$P_i = X_i P_i^\circ$$

where P_i° is the vapor pressure (at a given temperature) of pure substance i, X_i is its mole fraction in solution, and P_i is its partial vapor pressure over the solution. This is a generalization of Raoult's law to each component of a solution.

For an ideal mixture of two volatile substances, the vapor pressure of component 1 is

$$P_1 = X_1 P_1^\circ$$

and that of component 2 is

$$P_2 = X_2 P_2^\circ = (1 - X_1)P_2^\circ$$

The vapor pressures for such an ideal solution are shown in Figure 11.15, together with typical vapor pressures for a solution that shows positive deviations from ideal behavior.

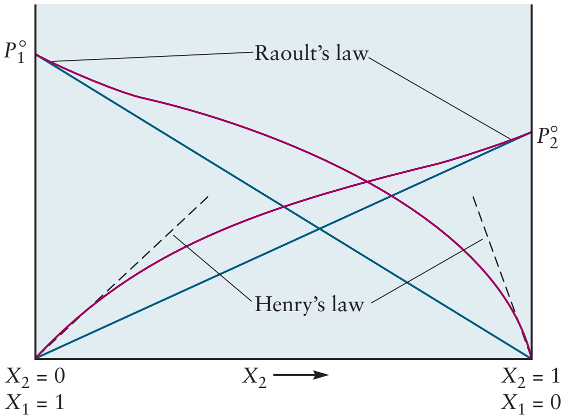


FIGURE 11.15 Vapor pressures above a mixture of two volatile liquids. Both ideal (blue lines) and nonideal behaviors (red curves) are shown. Positive deviations from ideal solution behavior are illustrated, although negative deviations are observed for other nonideal solutions. Raoult's and Henry's laws are shown as dilute solution limits for the nonideal mixture; the markers explicitly identify regions where Raoult's law and Henry's law represent actual behavior.

Henry's Law

At sufficiently low mole fraction X_2, the vapor pressure of component 2 (even in a nonideal solution) is proportional to X_2:

$$P_2 = k_2X_2 \tag{11.11}$$

where k_2 is a constant. For X_1 small (X_2 near 1),

$$P_1 = k_1X_1 = k_1(1 - X_2)$$

This linear vapor pressure of what is called the solute (because it is present at small mole fraction) is known as **Henry's law:** The vapor pressure of a volatile dissolved substance is proportional to the mole fraction of that substance in solution. Whenever Raoult's law is valid for a solvent, Henry's law is valid for the solute (see Fig. 11.15).

One familiar application of Henry's law is in the carbonation of beverages. If the partial pressure of CO_2 above a solution is increased, the amount dissolved in the solution increases proportionately. When the beverage can is opened, dissolved gas bubbles out of solution in response to the lower CO_2 pressure outside. Henry's law is important in biology, where gases such as oxygen dissolve in blood and other bodily fluids, and in environmental chemistry, where volatile pollutants can move between bodies of water and the atmosphere.

EXAMPLE 11.17

The Henry's law constant for oxygen dissolved in water is 4.34×10^4 atm at 25°C. If the partial pressure of oxygen in air is 0.20 atm under ordinary atmospheric conditions, calculate the concentration (in moles per liter) of dissolved oxygen in water that is in equilibrium with air at 25°C.

SOLUTION

Henry's law is used to calculate the mole fraction of oxygen in water:

$$X_{O_2} = \frac{P_{O_2}}{k_{O_2}} = \frac{0.20 \text{ atm}}{4.34 \times 10^4 \text{ atm}} = 4.6 \times 10^{-6}$$

Next, the mole fraction is converted to molarity. One liter of water weighs 1000 g, so it contains

$$\frac{1000 \text{ g } H_2O}{18.02 \text{ g mol}^{-1}} = 55.5 \text{ mol water}$$

Because X_{O_2} is so small, $n_{H_2O} + n_{O_2}$ is close to n_{H_2O}, and it can be written as

$$X_{O_2} = \frac{n_{O_2}}{n_{H_2O} + n_{O_2}} \approx \frac{n_{O_2}}{n_{H_2O}}$$

$$4.6 \times 10^{-6} = \frac{n_{O_2}}{55.5 \text{ mol}}$$

Thus, the number of moles of oxygen in 1 L water is

$$n_{O_2} = (4.6 \times 10^{-6})(55.5 \text{ mol}) = 2.6 \times 10^{-4} \text{ mol}$$

and the concentration of dissolved O_2 is 2.6×10^{-4} M.

Related Problems: 57, 58

Distillation

The vapor pressures of the pure components of an ideal solution usually differ, and for this reason, such a solution has a composition different from that of the vapor phase with which it is in equilibrium. This can best be seen in an example.

Hexane (C_6H_{14}) and heptane (C_7H_{16}) form a nearly ideal solution over the whole range of mole fractions. At 25°C, the vapor pressure of pure hexane is $P_1^\circ = 0.198$ atm, and that of pure heptane is $P_2^\circ = 0.0600$ atm. Suppose a solution contains 4.00 mol of hexane and 6.00 mol of heptane, and that its mole fractions are, therefore, $X_1 = 0.400$ and $X_2 = 0.600$. The vapor in equilibrium with this ideal solution has partial pressures

$$P_{\text{hexane}} = P_1 = X_1P_1^\circ = (0.400)(0.198 \text{ atm}) = 0.0792 \text{ atm}$$

$$P_{\text{heptane}} = P_2 = X_2P_2^\circ = (0.600)(0.0600 \text{ atm}) = 0.0360 \text{ atm}$$

From Dalton's law, the total pressure is the sum of these partial pressures:

$$P_{\text{total}} = P_1 + P_2 = 0.1152 \text{ atm}$$

If X_1' and X_2' are the mole fractions in the vapor, then

$$X_1' = \frac{0.0792 \text{ atm}}{0.1152 \text{ atm}} = 0.688$$

$$X_2' = 1 - X_1' = \frac{0.0360 \text{ atm}}{0.1152 \text{ atm}} = 0.312$$

The liquid and the vapor with which it is in equilibrium have different compositions (Fig. 11.16), and the vapor is enriched in the more volatile component.

Suppose some of this vapor is removed and condensed to a liquid. The vapor in equilibrium with this new solution would be still richer in the more volatile component, and the process could be continued further (see Fig. 11.16). This progression underlies the technique of separating a mixture into its pure components by **fractional distillation,** a process in which the components are successively evaporated and recondensed. What we have described so far corresponds to a constant-temperature process, but actual distillation is conducted at constant total pressure. The vapor pressure–mole fraction plot is transformed into a boiling temperature–mole fraction plot (Fig. 11.17). Note that the component with the lower vapor pressure (component 2) has the higher boiling point, T_b^2. If the temperature of a solution of a certain composition is raised until it touches the liquid line in the plot, the vapor in equilibrium with the solution is richer in the more volatile component 1. Its composition lies at the intersection of the horizontal constant-temperature line and the equilibrium vapor curve.

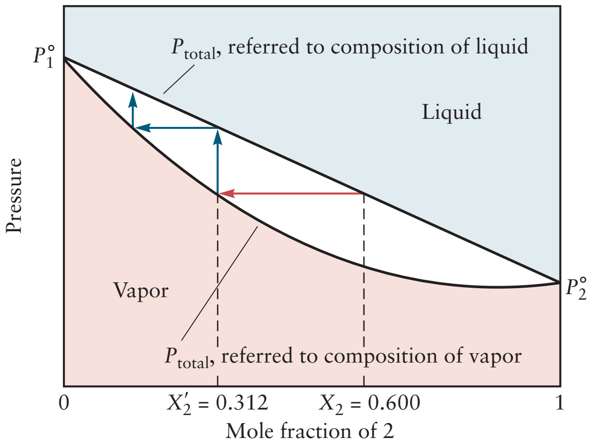


FIGURE 11.16 The composition of the vapor above a solution differs from the composition of the liquid with which it is in equilibrium. Here, the upper (straight) line is the total pressure of the vapor in equilibrium with an ideal solution having mole fraction X_2 of component 2. By moving horizontally from that line to a point of intersection with the lower curve, we can locate the mole fraction X_2' of component 2 in the vapor (red arrow). Subsequent condensations and vaporizations are shown by blue arrows.

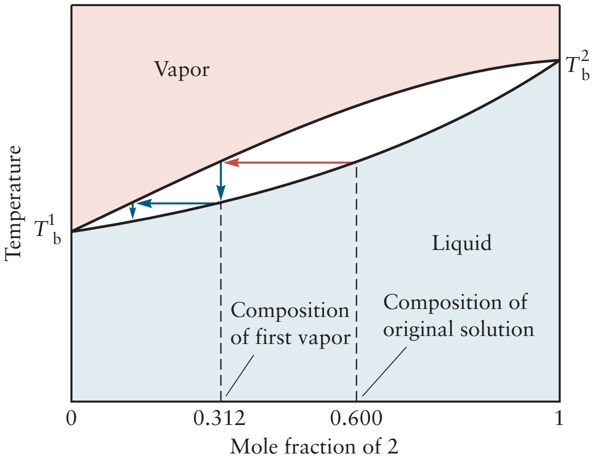


FIGURE 11.17 The boiling point of an ideal solution varies with the composition of the solution. The upper curve is the boiling temperature referred to the vapor composition, and the lower curve is the boiling temperature referred to the liquid composition. The vapors boiling off a solution that has a 0.600-mol fraction of component 2 are enriched in the more volatile component 1 to the extent that their mole fraction of component 2 is only 0.312 (red arrow). The subsequent blue arrows show the further steps used in obtaining nearly pure component 1 by fractional distillation.

A liquid can be vaporized in different ways. It can simply be boiled until it is entirely vaporized and the final composition of the vapor is the same as that of the original liquid. It is clear that such a mixture boils over a range of temperatures, rather than at a single T_b like a pure liquid. Alternatively, if the boiling is stopped midway, the vapor fraction that has boiled off can be collected and recondensed. The resulting liquid (the condensate) will be richer in component 1 than was the original solution. By repeating the process again and again, mixtures successively richer in component 1 will be obtained. This is the principle behind the **distillation column** (Fig. 11.18). Throughout the length of the tube, such evaporations and recondensations take place, and this allows mixtures to be separated into their constituent substances. Such a process is used to separate nitrogen and oxygen in air; the air is liquefied and then distilled, with the lower boiling nitrogen ($T_b = -196°C$) vaporizing before the oxygen ($T_b = -183°C$).

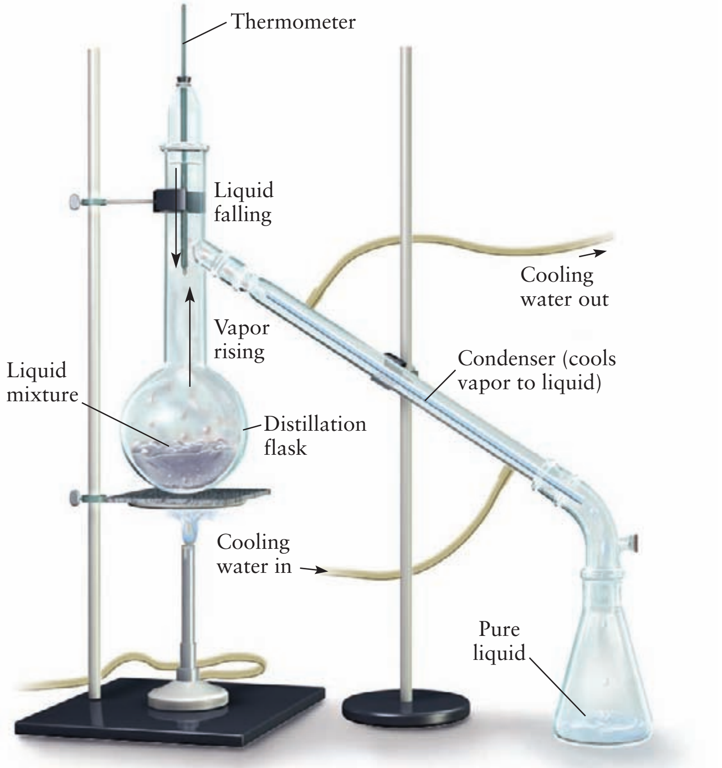
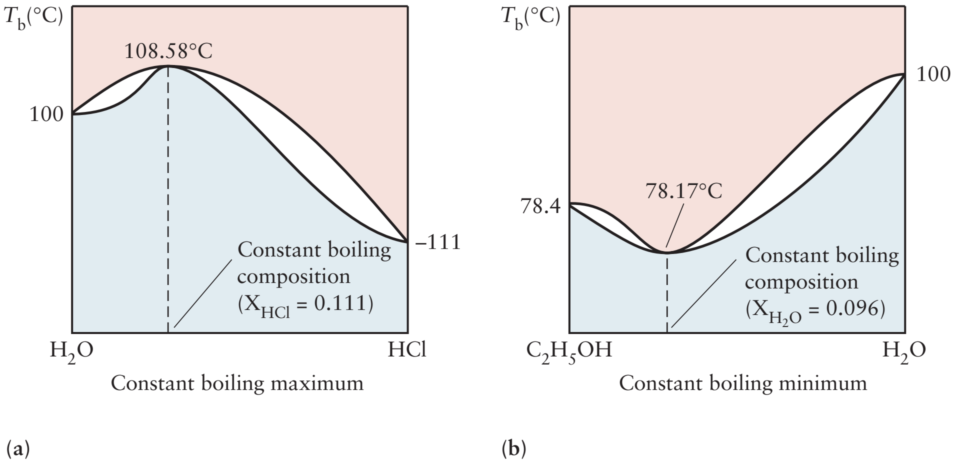


FIGURE 11.18 In a distillation column, temperature decreases with height in the column. The less volatile components condense and fall back to the flask, but the more volatile ones continue up the column into the water-cooled condenser, where they condense and are recovered in the receiver.

FIGURE 11.19 Dependence of boiling temperature on mole fraction for (a) maximum- and (b) minimum-boiling azeotropes. The coordinates are not to scale.



Nonideal solutions may have more complicated behavior. A mixture showing large *negative* deviations from Raoult's law (one in which solute–solvent forces are strongly attractive) will show a boiling-point *maximum* (Fig. 11.19a). A solution at the maximum is called a **maximum-boiling azeotrope;** an example is that formed by the H_2O/HCl system. The boiling-point maximum occurs in this case at 108.58°C and 1 atm pressure for a composition of 20.22% HCl by mass. A mixture showing large *positive* deviations from ideal behavior may show a boiling-point *minimum* (see Fig. 11.19b) and a corresponding **minimum-boiling azeotrope.** Ethanol and water form such an azeotrope with a normal boiling point of 78.17°C and a composition of 4% water by mass. In this case, attractive forces between ethanol molecules and between water molecules are stronger than those between ethanol and water, so the solution boils at a lower temperature than either pure component. An azeotrope behaves like a single-component fluid in that it boils at a well-defined temperature and the solution and vapor have the same composition. A mixture of two substances that form an azeotrope cannot be separated by fractional distillation into two pure substances, but rather into only one pure substance and a mixture with the azeotropic composition. A mixture of 50% ethanol and water, for example, can be distilled to obtain pure water and an azeotropic mixture containing 4% water and 96% ethanol. The last 4% of water cannot be removed by distillation at atmospheric pressure to obtain pure ethanol.

11.7 Colloidal Suspensions

A **colloid** is a mixture of two or more substances in which one phase is suspended as a large number of small particles in a second phase. The dispersed substance and the background medium may be any combination of gas, liquid, or solid. Examples of colloids include aerosol sprays (liquid suspended in gas), smoke (solid particles in air), milk (fat droplets and solids in water), mayonnaise (water droplets in oil), and paint (solid pigment particles in oil for oil-based paints, or pigment and oil dispersed in water for latex paints). Colloidal particles are larger than single molecules, but are too small to be seen by the eye; their dimensions typically range from 10^{-9} to 10^{-6} m in diameter. Their presence can be seen most dramatically in the way in which they scatter light; a familiar example is the passage of light from a movie projector through a suspension of small dust particles in air. The gemstone opal has remarkable optical properties that arise from colloidal water suspended in solid silicon dioxide (Fig. 11.20).


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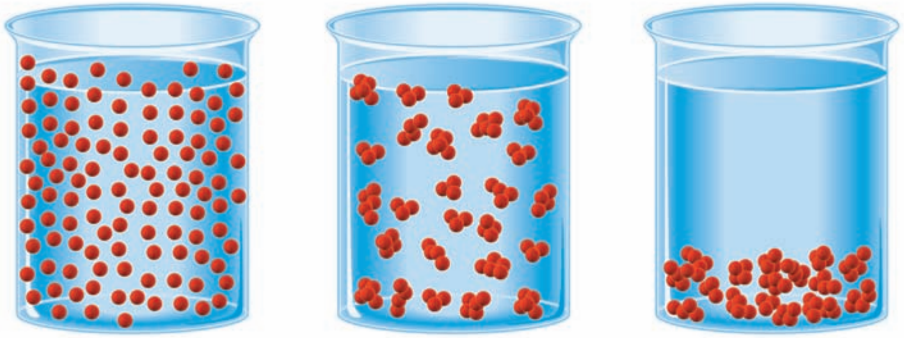
FIGURE 11.20 A natural opal.

Although some colloids settle out into two separate phases if left standing long enough, others persist indefinitely; a suspension of gold particles prepared by

FIGURE 11.21 When a salt is added to a colloidal dispersion (a), the repulsive forces between the colloidal particles are reduced and aggregation occurs (b). Eventually, the aggregated particles fall to the bottom of the container as low-density sediment (c).



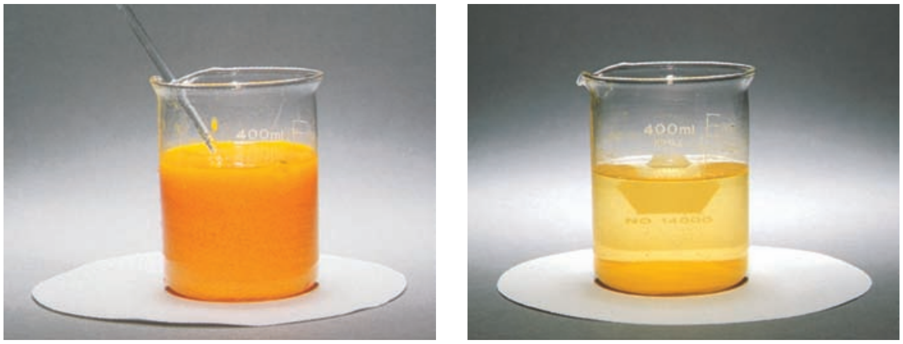
(a) Dispersion (b) Aggregation (c) Sedimentation

Michael Faraday in 1857 shows no apparent settling to date. In many colloids, the particles have net positive or negative charges on their surfaces, balanced by an opposite charge of ions in solution. The settling out of such colloids is speeded by dissolving salts in the solution, a process called **flocculation.** The salts reduce the repulsive electrostatic forces between the suspended particles, causing aggregation and sedimentation (Fig. 11.21). Flocculation occurs in river deltas; when river water containing suspended clay particles meets the salt water of the ocean, the clay settles out as open, low-density sediments. Flocculating agents are deliberately added to paints so that the pigment will settle in a loosely packed sediment. When the paint is stirred, the pigment is redispersed through the medium. In the absence of such agents, the suspended particles tend to settle in compact sediments that are difficult to resuspend.

In some cases, the formation of a colloid is not desirable, as in the precipitation of a solid from solution (see Section 11.2). Especially with metal sulfides, the solid precipitate may appear as a colloidal suspension with particles small enough to pass through ordinary filter paper (Fig. 11.22). If this happens, precipitated solid can be separated out only by flocculation, centrifugation, or forcing the suspension through a membrane, such as cellophane, that permits passage of only the small solvent molecules.

Suspended particles are in a constant state of motion, called **Brownian motion** after Robert Brown, a Scottish botanist who used a microscope to observe the motion of pollen particles in water. Brownian motion results from the constant random buffeting of the particles by solvent molecules. In 1905, Albert Einstein showed how the motion of Brownian particles could be described on a microscopic level; his work provided one of the most striking and convincing verifications of the molecular hypothesis and of the kinetic theory of matter and led to a fairly accurate determination of Avogadro's number.

FIGURE 11.22 (a) This colloidal suspension of $PbCrO_4$ appears cloudy. (b) After flocculation, the precipitate settles to the bottom.



(a) (b)

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CHAPTER SUMMARY

When pure substance A is mixed with pure substance B, the resulting solution has properties different from those of the pure substances because the intermolecular forces around each molecule are now quite different. In aqueous solutions, the dissolved species are described as solute ions or molecules surrounded by solvation shells of solvent molecules held in place by hydrogen bonding or ion–dipole forces. Solutions can be in equilibrium in solid, liquid, or vapor phases, but the conditions under which phases coexist are different from those for the pure solvent. Changes in vapor pressure, freezing point, boiling point, and osmotic pressure are explained quantitatively by the number of non-volatile solute species in the solution. When both species are volatile, the composition of the vapor phase is different from the composition of the solution, as described by Raoult's law and Henry's law, and the solution components can be separated by distillation. Many chemical reactions are carried out in liquid solutions, frequently by mixing solutions of the reactants. We write balanced chemical equations to describe the stoichiometry of reactions in solutions, and we count the number of moles of each reactant in a volume of solution through its concentration expressed in molarity. Solution stoichiometry describes many practical applications in acid–base and redox chemistry and is the basis for quantitative analytical techniques in these fields.

CUMULATIVE EXERCISE

Maple Syrup

The sap in a maple tree can be described as an approximately 3.0% (by mass) solution of sucrose ($C_{12}H_{22}O_{11}$) in water. Sucrose does not dissociate to any significant extent in aqueous solution.

(a) At 20°C, the density of sap is 1.010 g cm^{-3}. Calculate the molarity of sucrose in sap.

(b) A typical maple tree yields about 12 gallons of sap per year. Calculate how many grams of sucrose are contained in this volume of sap (1 gallon = 3.785 L).

(c) The rising of sap in trees is caused largely by osmosis; the concentration of dissolved sucrose in sap is higher than that of the groundwater outside the tree. Calculate the osmotic pressure of a sap solution and the height to which the sap should rise above the ground on a day when the temperature is 20°C. Approximate the groundwater as pure (although, in fact, it typically contains 0.01 to 0.03 M dissolved species). Express the answer in meters and in feet (1 m = 3.28 ft).

(d) To produce maple syrup from sap, the sap is boiled to reduce its water content. Calculate the normal boiling point of a sap solution.

(e) Maple syrup is the concentrated sap solution that results when most of the water is boiled off. The syrup has a composition of approximately 64% (by mass) sucrose and 36% water, with flavoring components present in small concentrations. If the density of the maple syrup is 1.31 g cm^{-3}, calculate the mole fraction, molarity, and molality of sucrose in maple syrup.

(f) What volume (in gallons) of maple syrup can be obtained from the sap in one typical tree?

(g) In the presence of vanadium(V) oxide, dinitrogen tetroxide oxidizes sucrose to oxalic acid ($H_2C_2O_4$) according to the following equation:

$$C_{12}H_{22}O_{11}(aq) + 9\ N_2O_4(s) \longrightarrow 6\ H_2C_2O_4(aq) + 18\ NO(g) + 5\ H_2O(\ell)$$

Calculate the mass of N_2O_4 that will react completely with 7.00 L of the sap solution from part (a), and give the concentration of oxalic acid that results.


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Tapping syrup from sugar maple trees.

Answers

(a) 0.089 M

(b) 1.4×10^3 g sucrose

(c) $\pi = 2.1$ atm; height = 22 m = 72 ft

(d) 100.046°C

(e) Mole fraction = 0.086; molarity = 2.4 M; molality = 5.2 mol kg^{-1}

(f) 0.56 gallon

(g) 5.2×10^2 g N_2O_4; 0.53 M

CHAPTER REVIEW

Solutions are described by their composition and method of preparation.

- Mole fraction: $X_i = n_i/n_{\text{tot}}$ where n_i is the number of moles of component *i* and n_{tot} is the total number of moles of all components
- Molarity: M = moles of solute per liter of solution
- Molality: *m* = moles of solute per kg of solvent
- For *dilute, aqueous* solutions $m \approx$ M
- Special procedures have been defined to prepare solutions of desired *X*, M, or *m*.

Solutions are formed by breaking the bonds between molecules or ions in the solute and dispersing these species throughout the solvent.

- The solute species are surrounded by solvent molecules, and experience very different intermolecular forces than in their pure, undissolved state.
- When water is the solvent the solution is called *aqueous* and solutes are labeled (*aq*).
- Ionic solutes dissociate in solution, whereas molecular solutes remain intact when dispersed in solution.
- Energy is required to disrupt the structure of the pure solute and solvent, and energy is released due to the attractive interactions between the solute and solvent. Formation of a solution can be endothermic or exothermic, depending on the difference between these energies.
- In aqueous solutions, solute species are surrounded by solvation shells of solvent molecules held in place by intermolecular forces, primarily hydrogen bonding and ion–dipole forces.

In this chapter we use the Arrhenius definition of acids and bases.

- An *acid* donates one or more protons when dissolved in water.
- A *base* donates one or more hydroxide ions when dissolved in water.
- In the neutralization reaction $\text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + H_2O$, OH^- is the base and H^+ is the acid. The net reaction is $H^+ + OH^- \longrightarrow H_2O$.

Acid–base titration is an analytical technique for finding the concentration of acid or base in an unknown solution.

- Stoichiometry of reactions in solutions is described by balanced equations that relate the number of moles of each reactant and product. The number of moles of each reaction species in a volume of solution is given by $n_i = \text{M}_i V$.
- Both neutralization reactions and dilution operations are described by $\text{M}_1 V_1 = \text{M}_2 V_2$.
- In titrations a measured volume of a solution with known M reacts to neutralize a known volume of sample whose M is unknown. The end point, at which neutralization is achieved, is signified by an endpoint indicator, most often a color change. At the end point, we determine the molarity of the unknown sample using the earlier equation.

In oxidation–reduction (redox) reactions electrons are transferred between reacting species as they combine to form products.

- Reactants that lose electrons are oxidized.

- Reactants that gain electrons are reduced.
- These reactions are coupled; it is not possible to have oxidation without reduction and vice versa.
- Balancing the equations for redox reactions involves special procedures. The steps are:
  - Assign oxidation numbers as described in Section 3.10.
  - Write unbalanced half-equations for the species being oxidized and the species being reduced.
  - Balance all atoms except oxygen and hydrogen.
  - Determine whether the reaction takes place in acidic or basic solution.
  - In acidic solution, add one H_3O^+ to the side that needs an extra H atom and then H_2O to the other side.
  - In basic solution, add one H_2O to the side that needs an extra H atom and then OH^- to the other side.
  - Balance charge transfer in each half-equation by inserting electrons as reactants or products.
  - Multiply the two half-equations by numbers that make the number of electrons given off in oxidation the same as the number gained in reduction.
  - Add the two half-equations together.

Like pure substances, solutions can have solid, liquid, and gaseous phases in equilibrium with one another.

- The conditions where phases coexist—such as boiling points, freezing points, and vapor pressure—have different values in solution than in the pure solvent.
- The colligative properties of solutions describe how nonvolatile solvents cause these changes in properties of the solvent. These changes depend only on the number of solute particles, not on their nature.
  - Vapor pressure lowering, boiling point elevation, freezing point depression and osmotic pressure are all treated with *empirical* equations.
  - Vapor pressure lowering: $\Delta P_1 = -X_2 P_1^\circ$ where X_2 is the mole fraction of the solute and P_1° is the vapor pressure of the pure solvent.
  - Boiling point elevation: $\Delta T = mK_b$ (the constants have been tabulated)
  - Freezing point depression: $\Delta T = -mK_f$ (the constants have been tabulated)
  - A solution in contact with its pure solvent across a semi-permeable membrane experiences an increase in pressure as pure solvent flows through the membrane into the solution. This osmotic pressure can be measured quite accurately, and through the equation $\pi V = nRT$ permits determination of the molecular weight of the solute.

When the solute is volatile, the vapor pressure in equilibrium with the solution has contributions from both solute and solvent.

- Raoult's law: vapor pressure of the solvent $P_1 = X_1 P_1^\circ$
- Henry's law: vapor pressure of the solute $P_2 = X_2 k_2$
- The partial pressures of the solute and solvent in the vapor will be different from their concentrations in the solution. The vapor will be richer in the more volatile component than is the solution. The process of distillation exploits this fact to separate the components of the solution by heating the solution to the temperature where the more volatile component boils, removing the vapor, and condensing it to the liquid state.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Express the concentration of a solute in solution in units of mass percentage, molarity, molality, and mole fraction (Section 11.1, Problems 3–8).

2. Describe how a solution of a given molarity is prepared and the effect on dilution of molarity (Section 11.1, Problems 9–12).
3. Describe the formation of a solution in molecular terms by comparing intermolecular forces in the pure phases and in the solution (Section 11.2).
4. Calculate the number of moles of substances reacting during a solution-phase reaction such as acid–base titration (Section 11.3, Problems 15–26).
5. Balance equations for redox reactions in aqueous solution, using the half-reaction method, and calculate the concentrations of substances during redox titrations (Section 11.4, Problems 27–40).
6. Calculate the molar mass of a nonvolatile solute from the changes it causes in the colligative properties (vapor-pressure lowering, boiling-point elevation, freezing-point lowering, or osmotic pressure) of its dilute solution (Section 11.5, Problems 41–56).
7. Discuss the meaning of Henry's law and use it to calculate the solubilities of gases in liquids (Section 11.6, Problems 57–60).
8. Relate the total pressure and composition of the vapor in equilibrium with an ideal two-component solution to the composition of the solution and the vapor pressures of its pure components (Section 11.6, Problems 61–64).
9. Explain how distillation is used to separate the volatile components of a binary liquid solution (Section 11.6).
10. Describe the physical properties of a colloidal suspension (Section 11.7).

KEY EQUATIONS

$$X_1 = \frac{n_1}{n_1 + n_2}$$

$$X_2 = \frac{n_2}{n_1 + n_2} = 1 - X_1$$

(Section 11.1)

$$\text{molarity} = \frac{\text{moles solute}}{\text{liters solution}} = \text{mol L}^{-1}$$

(Section 11.1)

$$\text{molality} = \frac{\text{moles solute}}{\text{kilograms solvent}} = \text{mol kg}^{-1}$$

(Section 11.1)

$$c_{\text{f}} = \frac{\text{moles solute}}{\text{final solution volume}} = \frac{c_{\text{i}}V_{\text{i}}}{V_{\text{f}}}$$

(Section 11.1)

$$P_1 = X_1 P_1^{\circ}$$

(Section 11.5)

$$P_1 = P_1 - P_1^{\circ} = X_1 P_1^{\circ} - P_1^{\circ} = -X_2 P_1^{\circ}$$

(Section 11.5)

$$\Delta T_{\text{b}} = K_{\text{b}} m$$

(Section 11.5)

$$\Delta T_{\text{f}} = T_{\text{f}}' - T_{\text{f}} = -K_{\text{f}} m$$

(Section 11.5)

$$\pi = \rho g h$$

(Section 11.5)

$$\pi = cRT$$

(Section 11.5)

$$P_2 = k_2 X_2$$

(Section 11.6)

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

Composition of Solutions

1. A patient has a "cholesterol count" of 214. Like many blood-chemistry measurements, this result is measured in units of milligrams per deciliter (mg dL^{-}).

(a) Determine the molar concentration of cholesterol in this patient's blood, taking the molar mass of cholesterol to be $386.64 \text{ g mol}^{-1}$.

(b) Estimate the molality of cholesterol in the patient's blood.

(c) If 214 is a typical cholesterol reading among men in the United States, determine the volume of such blood required to furnish 8.10 g of cholesterol.

2. In many states, a person is legally intoxicated if his or her blood has a concentration of 0.10 g (or more) of ethyl alcohol (C_2H_5OH) per deciliter. Express this "threshold concentration" in mol L^{-1}.

3. A solution of hydrochloric acid in water is 38.00% hydrochloric acid by mass. Its density is 1.1886 g cm^{-3} at 20°C. Compute its molarity, mole fraction, and molality at this temperature.

4. A solution of acetic acid and water contains 205.0 g L^{-1} of acetic acid and 820.0 g L^{-1} of water.

(a) Compute the density of the solution.

(b) Compute the molarity, molality, mole fraction, and mass percentage of acetic acid in this solution.

(c) Take the acetic acid as the solvent, and do the same for water as the solute.

5. A 6.0835 M aqueous solution of acetic acid ($C_2H_4O_2$) has a density of 1.0438 g cm^{-3}. Compute its molality.

6. A 1.241 M aqueous solution of $AgNO_3$ (used to prepare silver chloride photographic emulsions) has a density of 1.171 g cm^{-3}. Compute its molality.

7. Water is slightly soluble in liquid nitrogen. At −196°C (the boiling point of liquid nitrogen), the mole fraction of water in a saturated solution is 1.00×10^{-5}. Compute the mass of water that can dissolve in 1.00 kg of boiling liquid nitrogen.

8. Some water dissolves in liquid methane at −161°C to give a solution in which the mole fraction of water is 6.0×10^{-5}. Determine the mass of water dissolved in 1.00 L of this solution if the density of the solution is 0.78 g cm^{-3}.

9. Concentrated phosphoric acid as sold for use in the laboratory is usually 90% H_3PO_4 by mass (the rest is water). Such a solution contains 12.2 mol of H_3PO_4 per liter of solution at 25°C.

(a) Compute the density of this solution.

(b) What volume of this solution should be used in mixing 2.00 L of a 1.00 M phosphoric acid solution?

10. A perchloric acid solution is 60.0% $HClO_4$ by mass. It is simultaneously 9.20 M at 25°C.

(a) Compute the density of this solution.

(b) What volume of this solution should be used in mixing 1.00 L of a 1.00 M perchloric acid solution?

11. Suppose 25.0 g of solid NaOH is added to 1.50 L of an aqueous solution that is already 2.40 M in NaOH. Then water is added until the final volume is 4.00 L. Determine the concentration of the NaOH in the resulting solution.

12. Suppose 0.400 L of a solution of 0.0700 M nitric acid is added to 0.800 L of a solution of 0.0300 M nitric acid, giving a total volume of 1.200 L. Calculate the concentration (molarity) of nitric acid in the resulting solution.

Nature of Dissolved Species

13. Rewrite the following balanced equations as net ionic equations.

(a) $NaCl(aq) + AgNO_3(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$

(b) $K_2CO_3(s) + 2\,HCl(aq) \longrightarrow$
$2\,KCl(aq) + CO_2(g) + H_2O(\ell)(s) + 2\,H_2O(\ell)$

(c) $2\,Cs(s) + 2\,H_2O(\ell) \longrightarrow 2\,CsOH(aq) + H_2(g)$

(d) $2\,KMnO_4(aq) + 16\,HCl(aq) \longrightarrow$
$5\,Cl_2(g) + 2\,MnCl_2(aq) + 2\,KCl(aq) + 8\,H_2O(\ell)$

14. Rewrite the following balanced equations as net ionic equations.

(a) $Na_2SO_4(aq) + BaCl_2(aq) \longrightarrow BaSO_4(s) + 2\,NaCl(aq)$

(b) $6\,NaOH(aq) + 3\,Cl_2(g) \longrightarrow$
$NaClO_3(aq) + 5\,NaCl(aq) + 3\,H_2O(\ell)$

(c) $Hg_2(NO_3)_2(aq) + 2\,KI(aq) \longrightarrow Hg_2I_2(s) + 2\,KNO_3(aq)$

(d) $3\,NaOCl(aq) + KI(aq) \longrightarrow$
$NaIO_3(aq) + 2\,NaCl(aq) + KCl(aq)$

Reaction Stoichiometry in Solutions: Acid–Base Titrations

15. When treated with acid, lead(IV) oxide is reduced to a lead(II) salt, with the liberation of oxygen:

$$2\,PbO_2(s) + 4\,HNO_3(aq) \longrightarrow 2\,Pb(NO_3)_2(aq) + 2\,H_2O(\ell) + O_2(g)$$

What volume of a 7.91 M solution of nitric acid is just sufficient to react with 15.9 g of lead(IV) oxide, according to this equation?

16. Phosphoric acid is made industrially by the reaction of fluorapatite, $Ca_5(PO_4)_3F$, in phosphate rock with sulfuric acid:

$$Ca_5(PO_4)_3F(s) + 5\,H_2SO_4(aq) + 10\,H_2O(\ell) \longrightarrow 3\,H_3PO_4(aq) + 5\,(CaSO_4{\cdot}2H_2O)(s) + HF(aq)$$

What volume of 6.3 M phosphoric acid is generated by the reaction of 2.2 metric tons (2200 kg) of fluorapatite?

17. The carbon dioxide produced (together with hydrogen) from the industrial-scale oxidation of methane in the presence of nickel is removed from the gas mixture in a scrubber containing an aqueous solution of potassium carbonate:

$$CO_2(g) + H_2O(\ell) + K_2CO_3(aq) \longrightarrow 2\,KHCO_3(aq)$$

Calculate the volume of carbon dioxide (at 50°C and 1.00 atm pressure) that will react with 187 L of a 1.36 M potassium carbonate solution.

18. Nitrogen oxide can be generated on a laboratory scale by the reaction of dilute sulfuric acid with aqueous sodium nitrite:

$$6\ \mathrm{NaNO_2}(aq) + 3\ \mathrm{H_2SO_4}(aq) \longrightarrow 4\ \mathrm{NO}(g) + 2\ \mathrm{HNO_3}(aq) + 2\ \mathrm{H_2O}(\ell) + 3\ \mathrm{Na_2SO_4}(aq)$$

What volume of 0.646 M aqueous $\mathrm{NaNO_2}$ should be used in this reaction to generate 5.00 L of nitrogen oxide at a temperature of 20°C and a pressure of 0.970 atm?

19. Write a balanced equation for the acid–base reaction that leads to the production of each of the following salts. Name the acid, base, and salt.

(a) $\mathrm{CaF_2}$
(b) $\mathrm{Rb_2SO_4}$
(c) $\mathrm{Zn(NO_3)_2}$
(d) $\mathrm{KCH_3COO}$

20. Write a balanced equation for the acid–base reaction that leads to the production of each of the following salts. Name the acid, base, and salt.

(a) $\mathrm{Na_2SO_3}$
(b) $\mathrm{Ca(C_6H_5COO)_2}$
(c) $\mathrm{PbSO_4}$
(d) $\mathrm{CuCl_2}$

21. Hydrogen sulfide can be removed from natural gas by reaction with excess sodium hydroxide. Name the salt that is produced in this reaction. (**Note:** Hydrogen sulfide loses both its hydrogen atoms in the course of this reaction.)

22. During the preparation of viscose rayon, cellulose is dissolved in a bath containing sodium hydroxide and later reprecipitated as rayon using a solution of sulfuric acid. Name the salt that is a by-product of this process. Rayon production is, in fact, a significant commercial source for this salt.

23. Phosphorus trifluoride is a highly toxic gas that reacts slowly with water to give a mixture of phosphorous acid and hydrofluoric acid.

(a) Write a balanced chemical equation for this reaction.
(b) Determine the concentration (in moles per liter) of each of the acids that result from the reaction of 1.94 L of phosphorus trifluoride (measured at 25°C and 0.970 atm pressure) with water to give a solution volume of 872 mL.

24. Phosphorus pentachloride reacts violently with water to give a mixture of phosphoric acid and hydrochloric acid.

(a) Write a balanced chemical equation for this reaction.
(b) Determine the concentration (in moles per liter) of each of the acids that result from the complete reaction of 1.22 L of phosphorus pentachloride (measured at 215°C and 0.962 atm pressure) with enough water to give a solution volume of 697 mL.

25. To determine the concentration of a solution of nitric acid, a 100.0-mL sample is placed in a flask and titrated with a 0.1279 M solution of potassium hydroxide. A volume of 37.85 mL is required to reach the phenolphthalein end point. Calculate the concentration of nitric acid in the original sample.

26. The concentration of aqueous ammonia in a cleaning solution is determined by titration with hydrochloric acid. A volume of 23.18 mL of 0.8381 M HCl is needed to titrate a 50.0-mL sample of the ammonia solution to a methyl red end point. Calculate the concentration of ammonia in the cleaning solution.

Reaction Stoichiometry in Solutions: Oxidation–Reduction Titrations

27. For each of the following balanced equations, write the oxidation number above the symbol of each atom that changes oxidation state in the course of the reactions.

(a) $2\ \mathrm{PF_2I}(\ell) + 2\ \mathrm{Hg}(\ell) \longrightarrow \mathrm{P_2F_4}(g) + \mathrm{Hg_2I_2}(s)$
(b) $2\ \mathrm{KClO_3}(s) \longrightarrow 2\ \mathrm{KCl}(s) + 3\ \mathrm{O_2}(g)$
(c) $4\ \mathrm{NH_3}(g) + 5\ \mathrm{O_2}(g) \longrightarrow 4\ \mathrm{NO}(g) + 6\ \mathrm{H_2O}(g)$
(d) $2\ \mathrm{As}(s) + 6\ \mathrm{NaOH}(\ell) \longrightarrow 2\ \mathrm{Na_3AsO_3}(s) + 3\ \mathrm{H_2}(g)$

28. For each of the following balanced equations, write the oxidation number above the symbol of each atom that changes oxidation state in the course of the reaction.

(a) $\mathrm{N_2O_4}(g) + \mathrm{KCl}(s) \longrightarrow \mathrm{NOCl}(g) + \mathrm{KNO_3}(s)$
(b) $\mathrm{H_2S}(g) + 4\ \mathrm{O_2F_2}(s) \longrightarrow \mathrm{SF_6}(g) + 2\ \mathrm{HF}(g) + 4\ \mathrm{O_2}(g)$
(c) $2\ \mathrm{POBr_3}(s) + 3\ \mathrm{Mg}(s) \longrightarrow 2\ \mathrm{PO}(s) + 3\ \mathrm{MgBr_2}(s)$
(d) $4\ \mathrm{BCl_3}(g) + 3\ \mathrm{SF_4}(g) \longrightarrow 4\ \mathrm{BF_3}(g) + 3\ \mathrm{SCl_2}(\ell) + 3\ \mathrm{Cl_2}(g)$

29. Selenic acid ($\mathrm{H_2SeO_4}$) is a powerful oxidizing acid that dissolves not only silver (as does the related acid $\mathrm{H_2SO_4}$) but gold, through the following reaction:

$$2\ \mathrm{Au}(s) + 6\ \mathrm{H_2SeO_4}(aq) \longrightarrow \mathrm{Au_2(SeO_4)_3}(aq) + 3\ \mathrm{H_2SeO_3}(aq) + 3\ \mathrm{H_2O}(\ell)$$

Determine the oxidation numbers of the atoms in this equation. Which species is oxidized and which is reduced?

30. Diiodine pentaoxide oxidizes carbon monoxide to carbon dioxide under room conditions, yielding iodine as the second product:

$$\mathrm{I_2O_5}(s) + 5\ \mathrm{CO}(g) \longrightarrow \mathrm{I_2}(s) + 5\ \mathrm{CO_2}(g)$$

This can be used in an analytical method to measure the amount of carbon monoxide in a sample of air. Determine the oxidation numbers of the atoms in this equation. Which species is oxidized and which is reduced?

31. Complete and balance the following equations for reactions taking place in acidic solution.

(a) $\mathrm{VO_2^{+}}(aq) + \mathrm{SO_2}(g) \longrightarrow \mathrm{VO^{2+}}(aq) + \mathrm{SO_4^{2-}}(aq)$
(b) $\mathrm{Br_2}(\ell) + \mathrm{SO_2}(g) \longrightarrow \mathrm{Br^-}(aq) + \mathrm{SO_4^{2-}}(aq)$
(c) $\mathrm{Cr_2O_7^{2-}}(aq) + \mathrm{Np^{4+}}(aq) \longrightarrow \mathrm{Cr^{3+}}(aq) + \mathrm{NpO_2^{2+}}(aq)$
(d) $\mathrm{HCOOH}(aq) + \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{CO_2}(g) + \mathrm{Mn^{2+}}(aq)$
(e) $\mathrm{Hg_2HPO_4}(s) + \mathrm{Au}(s) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{Hg}(\ell) + \mathrm{H_2PO_4^-}(aq) + \mathrm{AuCl_4^-}(aq)$

32. Complete and balance the following equations for reactions taking place in acidic solution.

(a) $\mathrm{MnO_4^-}(aq) + \mathrm{H_2S}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + \mathrm{SO_4^{2-}}(aq)$
(b) $\mathrm{Zn}(s) + \mathrm{NO_3^-}(aq) \longrightarrow \mathrm{Zn^{2+}}(aq) + \mathrm{NH_4^+}(aq)$
(c) $\mathrm{H_2O_2}(aq) + \mathrm{MnO_4^-}(aq) \longrightarrow \mathrm{O_2}(g) + \mathrm{Mn^{2+}}(aq)$
(d) $\mathrm{Sn}(s) + \mathrm{NO_3^-}(aq) \longrightarrow \mathrm{Sn^{4+}}(aq) + \mathrm{N_2O}(g)$
(e) $\mathrm{UO_2^{2+}}(aq) + \mathrm{Te}(s) \longrightarrow \mathrm{U^{4+}}(aq) + \mathrm{TeO_4^{2-}}(aq)$

33. Complete and balance the following equations for reactions taking place in basic solution.

(a) $\mathrm{Cr(OH)_3}(s) + \mathrm{Br_2}(aq) \longrightarrow \mathrm{CrO_4^{2-}}(aq) + \mathrm{Br^-}(aq)$
(b) $\mathrm{ZrO(OH)_2}(s) + \mathrm{SO_3^{2-}}(aq) \longrightarrow \mathrm{Zr}(s) + \mathrm{SO_4^{2-}}(aq)$
(c) $\mathrm{HPbO_2^-}(aq) + \mathrm{Re}(s) \longrightarrow \mathrm{Pb}(s) + \mathrm{ReO_4^-}(aq)$
(d) $\mathrm{HXeO_4^-}(aq) \longrightarrow \mathrm{XeO_6^{4-}}(aq) + \mathrm{Xe}(g)$
(e) $\mathrm{N_2H_4}(aq) + \mathrm{CO_3^{2-}}(aq) \longrightarrow \mathrm{N_2}(g) + \mathrm{CO}(g)$

34. Complete and balance the following equations for reactions taking place in basic solution.

(a) $OCl^-(aq) + I^-(aq) \longrightarrow IO_3^-(aq) + Cl^-(aq)$
(b) $SO_3^{2-}(aq) + Be(s) \longrightarrow S_2O_3^{2-}(aq) + Be_2O_3^{2-}(aq)$
(c) $H_2BO_3^-(aq) + Al(s) \longrightarrow BH_4^-(aq) + H_2AlO_3^-(aq)$
(d) $O_2(g) + Sb(s) \longrightarrow H_2O_2(aq) + SbO_2^-(aq)$
(e) $Sn(OH)_6^{2-}(aq) + Si(s) \longrightarrow HSnO_2^-(aq) + SiO_3^{2-}(aq)$

35. The following balanced equations represent reactions that occur in aqueous acid. Break them down into balanced oxidation and reduction half-equations.

(a) $2\ H_3O^+(aq) + H_2O_2(aq) + 2\ Fe^{2+}(aq) \longrightarrow 2\ Fe^{3+}(aq) + 4\ H_2O(\ell)$
(b) $H_3O^+(aq) + H_2O(\ell) + 2\ MnO_4^-(aq) + 5\ SO_2(aq) \longrightarrow 2\ Mn^{2+}(aq) + 5\ HSO_4^-(aq)$
(c) $5\ ClO_2^-(aq) + 4\ H_3O^+(aq) \longrightarrow 4\ ClO_2(g) + Cl^-(aq) + 6\ H_2O(\ell)$

36. The following balanced equations represent reactions that occur in aqueous base. Break them down into balanced oxidation and reduction half-equations.

(a) $4\ PH_3(g) + 4\ H_2O(\ell) + 4\ CrO_4^{2-}(aq) \longrightarrow P_4(s) + 4\ Cr(OH)_4^-(aq) + 4\ OH^-(aq)$
(b) $NiO_2(s) + 2\ H_2O(\ell) + Fe(s) \longrightarrow Ni(OH)_2(s) + Fe(OH)_2(s)$
(c) $CO_2(g) + 2\ NH_2OH(aq) \longrightarrow CO(g) + N_2(g) + 3\ H_2O(g)$

37. Nitrous acid (HNO_2) disproportionates in acidic solution to nitrate ion (NO_3^-) and nitrogen oxide (NO). Write a balanced equation for this reaction.

38. Thiosulfate ion ($S_2O_3^{2-}$) disproportionates in acidic solution to give solid sulfur and aqueous hydrogen sulfite ion (HSO_3^-). Write a balanced equation for this reaction.

39. Potassium dichromate in acidic solution is used to titrate a solution of iron(II) ions, with which it reacts according to

$$Cr_2O_7^{2-}(aq) + 6\ Fe^{2+}(aq) + 14\ H_3O^+(aq) \longrightarrow 2\ Cr^{3+}(aq) + 6\ Fe^{3+}(aq) + 21\ H_2O(\ell)$$

A potassium dichromate solution is prepared by dissolving 5.134 g of $K_2Cr_2O_7$ in water and diluting to a total volume of 1.000 L. A total of 34.26 mL of this solution is required to reach the end point in a titration of a 500.0-mL sample containing $Fe^{2+}(aq)$. Determine the concentration of Fe^{2+} in the original solution.

40. Cerium(IV) ions are strong oxidizing agents in acidic solution, oxidizing arsenious acid to arsenic acid according to the following equation:

$$2\ Ce^{4+}(aq) + H_3AsO_3(aq) + 3\ H_2O(\ell) \longrightarrow 2\ Ce^{3+}(aq) + H_3AsO_4(aq) + 2\ H^+(aq)$$

A sample of As_2O_3 weighing 0.217 g is dissolved in basic solution and then acidified to make H_3AsO_3. Its titration with a solution of acidic cerium(IV) sulfate requires 21.47 mL. Determine the original concentration of $Ce^{4+}(aq)$ in the titrating solution.

Phase Equilibrium in Solutions: Nonvolatile Solutes

41. The vapor pressure of pure acetone (CH_3COCH_3) at 30°C is 0.3270 atm. Suppose 15.0 g of benzophenone, $C_{13}H_{10}O$, is dissolved in 50.0 g of acetone. Calculate the vapor pressure of acetone above the resulting solution.

42. The vapor pressure of diethyl ether (molar mass, 74.12 g mol^{-1}) at 30°C is 0.8517 atm. Suppose 1.800 g of maleic acid, $C_4H_4O_4$, is dissolved in 100.0 g of diethyl ether at 30°C. Calculate the vapor pressure of diethyl ether above the resulting solution.

43. Pure toluene (C_7H_8) has a normal boiling point of 110.60°C. A solution of 7.80 g of anthracene ($C_{14}H_{10}$) in 100.0 g of toluene has a boiling point of 112.06°C. Calculate K_b for toluene.

44. When 2.62 g of the nonvolatile solid anthracene, $C_{14}H_{10}$, is dissolved in 100.0 g of cyclohexane, C_6H_{12}, the boiling point of the cyclohexane is raised by 0.41°C. Calculate K_b for cyclohexane.

45. When 39.8 g of a nondissociating, nonvolatile sugar is dissolved in 200.0 g of water, the boiling point of the water is raised by 0.30°C. Estimate the molar mass of the sugar.

46. When 2.60 g of a substance that contains only indium and chlorine is dissolved in 50.0 g of tin(IV) chloride, the normal boiling point of the tin(IV) chloride is raised from 114.1°C to 116.3°C. If $K_b = 9.43$ K kg mol^{-1} for $SnCl_4$, what are the approximate molar mass and the probable molecular formula of the solute?

47. The Rast method for determining molar masses uses camphor as the solvent. Camphor melts at 178.4°C, and its large K_f (37.7 K kg mol^{-1}) makes it especially useful for accurate work. A sample of an unknown substance that weighs 0.840 g reduces the freezing point of 25.0 g of camphor to 170.8°C. What is its molar mass?

48. Barium chloride has a freezing point of 962°C and a freezing-point depression constant of 108 K kg mol^{-1}. If 12 g of an unknown substance dissolved in 562 g of barium chloride gives a solution with a freezing point of 937°C, compute the molar mass of the unknown, assuming no dissociation takes place.

49. Ice cream is made by freezing a liquid mixture that, as a first approximation, can be considered a solution of sucrose ($C_{12}H_{22}O_{11}$) in water. Estimate the temperature at which the first ice crystals begin to appear in a mix that consists of 34% (by mass) sucrose in water. As ice crystallizes out, the remaining solution becomes more concentrated. What happens to its freezing point?

50. The solution to Problem 49 shows that to make homemade ice cream, temperatures ranging downward from −3°C are needed. Ice cubes from a freezer have a temperature of about −12°C (+10°F), which is cold enough, but contact with the warmer ice cream mixture causes them to melt to liquid at 0°C, which is too warm. To obtain a liquid that is cold enough, salt (NaCl) is dissolved in water, and ice is added to the saltwater. The salt lowers the freezing point of the water enough so that it can freeze the liquid inside the ice cream maker. The instructions for an ice cream maker say to add one part salt to eight parts water (by mass). What is the freezing point of this solution (in degrees Celsius and degrees Fahrenheit)? Assume that the NaCl dissociates fully into ions, and that the solution is ideal.

51. An aqueous solution is 0.8402 molal in Na_2SO_4. It has a freezing point of -4.218°C. Determine the effective number of particles arising from each Na_2SO_4 formula unit in this solution.

52. The freezing-point depression constant of pure H_2SO_4 is 6.12 K kg mol^{-1}. When 2.3 g of ethanol (C_2H_5OH) is dissolved in 1.00 kg of pure sulfuric acid, the freezing point of the solution is 0.92 K lower than the freezing point of pure sulfuric acid. Determine how many particles are formed as 1 molecule of ethanol goes into solution in sulfuric acid.

53. A 200-mg sample of a purified compound of unknown molar mass is dissolved in benzene and diluted with that solvent to a volume of 25.0 cm^3. The resulting solution is found to have an osmotic pressure of 0.0105 atm at 300 K. What is the molar mass of the unknown compound?

54. Suppose 2.37 g of a protein is dissolved in water and diluted to a total volume of 100.0 mL. The osmotic pressure of the resulting solution is 0.0319 atm at 20°C. What is the molar mass of the protein?

55. A polymer of large molar mass is dissolved in water at 15°C, and the resulting solution rises to a final height of 15.2 cm above the level of the pure water, as water molecules pass through a semipermeable membrane into the solution. If the solution contains 4.64 g polymer per liter, calculate the molar mass of the polymer.

56. Suppose 0.125 g of a protein is dissolved in 10.0 cm^3 of ethyl alcohol (C_2H_5OH), whose density at 20°C is 0.789 g cm^{-3}. The solution rises to a height of 26.3 cm in an osmometer (an apparatus for measuring osmotic pressure). What is the approximate molar mass of the protein?

Phase Equilibrium in Solutions: Volatile Solutes

57. The Henry's law constant at 25°C for carbon dioxide dissolved in water is 1.65×10^3 atm. If a carbonated beverage is bottled under a CO_2 pressure of 5.0 atm:

(a) Calculate the number of moles of carbon dioxide dissolved per liter of water under these conditions, using 1.00 g cm^{-3} as the density of water.

(b) Explain what happens on a microscopic level after the bottle cap is removed.

58. The Henry's law constant at 25°C for nitrogen dissolved in water is 8.57×10^4 atm, that for oxygen is 4.34×10^4 atm, and that for helium is 1.7×10^5 atm.

(a) Calculate the number of moles of nitrogen and oxygen dissolved per liter of water in equilibrium with air at 25°C. Use Table 9.1.

(b) Air is dissolved in blood and other bodily fluids. As a deep-sea diver descends, the pressure increases and the concentration of dissolved air in the blood increases. If the diver returns to the surface too quickly, gas bubbles out of solution within the body so rapidly that it can cause a dangerous condition called "the bends." Use Henry's law to show why divers sometimes use a combination of helium and oxygen in their breathing tanks in place of compressed air.

59. At 25°C, some water is added to a sample of gaseous methane (CH_4) at 1.00 atm pressure in a closed vessel, and the vessel is shaken until as much methane as possible dissolves. Then 1.00 kg of the solution is removed and boiled to expel the methane, yielding a volume of 3.01 L of $CH_4(g)$ at 0°C and 1.00 atm. Determine the Henry's law constant for methane in water.

60. When exactly the procedure of Problem 59 is conducted using benzene (C_6H_6) in place of water, the volume of methane that results is 0.510 L at 0°C and 1.00 atm. Determine the Henry's law constant for methane in benzene.

61. At 20°C, the vapor pressure of toluene is 0.0289 atm and the vapor pressure of benzene is 0.0987 atm. Equal numbers of moles of toluene and benzene are mixed and form an ideal solution. Compute the mole fraction of benzene in the vapor in equilibrium with this solution.

62. At 90°C, the vapor pressure of toluene is 0.534 atm and the vapor pressure of benzene is 1.34 atm. Benzene (0.400 mol) is mixed with toluene (0.900 mol) to form an ideal solution. Compute the mole fraction of benzene in the vapor in equilibrium with this solution.

63. At 40°C, the vapor pressure of pure carbon tetrachloride (CCl_4) is 0.293 atm and the vapor pressure of pure dichloroethane ($C_2H_4Cl_2$) is 0.209 atm. A nearly ideal solution is prepared by mixing 30.0 g of carbon tetrachloride with 20.0 g of dichloroethane.

(a) Calculate the mole fraction of CCl_4 in the solution.

(b) Calculate the total vapor pressure of the solution at 40°C.

(c) Calculate the mole fraction of CCl_4 in the vapor in equilibrium with the solution.

64. At 300 K, the vapor pressure of pure benzene (C_6H_6) is 0.1355 atm and the vapor pressure of pure *n*-hexane (C_6H_{14}) is 0.2128 atm. Mixing 50.0 g of benzene with 50.0 g of *n*-hexane gives a solution that is nearly ideal.

(a) Calculate the mole fraction of benzene in the solution.

(b) Calculate the total vapor pressure of the solution at 300 K.

(c) Calculate the mole fraction of benzene in the vapor in equilibrium with the solution.

ADDITIONAL PROBLEMS

65. Veterinarians use Donovan's solution to treat skin diseases in animals. The solution is prepared by mixing 1.00 g of $AsI_3(s)$, 1.00 g of $HgI_2(s)$, and 0.900 g of $NaHCO_3(s)$ in enough water to make a total volume of 100.0 mL.

(a) Compute the total mass of iodine per liter of Donovan's solution, in grams per liter.

(b) You need a lot of Donovan's solution to treat an outbreak of rash in an elephant herd. You have plenty of mercury(II) iodide and sodium hydrogen carbonate, but the only arsenic(III) iodide you can find is 1.50 L of a 0.100 M aqueous solution. Explain how to prepare 3.50 L of Donovan's solution starting with these materials.

66. Relative solubilities of salts in liquid ammonia can differ significantly from those in water. Thus, silver bromide is soluble in ammonia, but barium bromide is not (the reverse of the situation in water).

(a) Write a balanced equation for the reaction of an ammonia solution of barium nitrate with an ammonia solution of silver bromide. Silver nitrate is soluble in liquid ammonia.

(b) What volume of a 0.50 M solution of silver bromide will react completely with 0.215 L of a 0.076 M solution of barium nitrate in ammonia?

(c) What mass of barium bromide will precipitate from the reaction in part (b)?

* 67. A 5.0-L flask contains a mixture of ammonia and nitrogen at 27°C and a total pressure of 3.00 atm. The sample of gas is allowed to flow from the flask until the pressure in the flask has fallen to 1.00 atm. The gas that escapes is passed through 1.50 L of 0.200 M acetic acid. All the ammonia in the gas that escapes is absorbed by the solution and turns out to be just sufficient to neutralize the acetic acid present. The volume of the solution does not change significantly.

(a) Will the electrical conductivity of the aqueous solution change significantly as the gas is absorbed? Give equations for any reactions, and calculate the final concentrations of the principal ions present (if any) at the end.

(b) Calculate the percentage by mass of ammonia in the flask initially.

* 68. It was desired to neutralize a certain solution X that had been prepared by mixing solutions of potassium chloride and hydrobromic acid. Titration of 10.0 mL X with 0.100 M silver nitrate required 50.0 mL of the latter. The resulting precipitate, containing a mixture of AgCl and AgBr, was dried and found to weigh 0.762 g. How much 0.100 M sodium hydroxide should be used to neutralize 10.0 mL solution X?

* 69. Vanadic ion, V^{3+}, forms green salts and is a good reducing agent, being itself changed in neutral solutions to the nearly colorless ion $V(OH)_4^+$. Suppose that 15.0 mL of a 0.200-M solution of vanadic sulfate, $V_2(SO_4)_3$, was needed to reduce completely a 0.540-g sample of an unknown substance X. If each molecule of X accepted just one electron, what is the molecular weight of X? Suppose that each molecule of X accepted three electrons; what would be the molecular weight of X then?

* 70. A new antibiotic, A, which is an acid, can readily be oxidized by hot aqueous permanganate; the latter is reduced to manganous ion, Mn^{2+}. The following experiments have been performed with A: (a) 0.293 g A consumes just 18.3 mL of 0.080 M $KMnO_4$; (b) 0.385 g A is just neutralized by 15.7 mL of 0.490 M NaOH. What can you conclude about the molecular weight of A from (a), from (b), and from both considered together?

71. Suppose 150 mL of a 10.00% by mass solution of sodium chloride (density = 1.0726 g cm^{-3}) is acidified with sulfuric acid and then treated with an excess of $MnO_2(s)$. Under these conditions, all the chlorine is liberated as $Cl_2(g)$. The chlorine is collected without loss and reacts with excess $H_2(g)$ to form $HCl(g)$. The $HCl(g)$ is dissolved in enough water to make 250 mL of solution. Compute the molarity of this solution.

* 72. The amount of ozone in a mixture of gases can be determined by passing the mixture through an acidic aqueous solution of potassium iodide, where the ozone reacts according to

$$O_3(g) + 3\,I^-(aq) + H_2O(\ell) \longrightarrow O_2(g) + I_3^-(aq) + 2\,OH^-(aq)$$

to form the triiodide ion I_3^-. The amount of triiodide produced is then determined by titrating with thiosulfate solution:

$$I_3^-(aq) + 2\,S_2O_3^{2-}(aq) \longrightarrow 3\,I^-(aq) + S_4O_6^{2-}(aq)$$

A small amount of starch solution is added as an indicator because it forms a deep-blue complex with the triiodide solution. Disappearance of the blue color thus signals the completion of the titration. Suppose 53.2 L of a gas mixture at a temperature of 18°C and a total pressure of 0.993 atm is passed through a solution of potassium iodide until the ozone in the mixture has reacted completely. The solution requires 26.2 mL of a 0.1359-M solution of thiosulfate ion to titrate to the endpoint. Calculate the mole fraction of ozone in the original gas sample.

73. The vapor pressure of pure liquid CS_2 is 0.3914 atm at 20°C. When 40.0 g of rhombic sulfur is dissolved in 1.00 kg of CS_2, the vapor pressure of CS_2 decreases to 0.3868 atm. Determine the molecular formula for the sulfur molecules dissolved in CS_2.

74. The expressions for boiling-point elevation and freezing-point depression apply accurately to *dilute* solutions only. A saturated aqueous solution of NaI (sodium iodide) in water has a boiling point of 144°C. The mole fraction of NaI in the solution is 0.390. Compute the molality of this solution. Compare the boiling-point elevation predicted by the expression in this chapter with the elevation actually observed.

75. You take a bottle of soft drink out of your refrigerator. The contents are liquid and stay liquid, even when you shake them. Presently, you remove the cap and the liquid freezes solid. Offer a possible explanation for this observation.

76. Mercury(II) chloride ($HgCl_2$) freezes at 276.1°C and has a freezing-point depression constant K_f of 34.3 K kg mol^{-1}. When 1.36 g of solid mercury(I) chloride (empirical formula HgCl) is dissolved in 100 g of $HgCl_2$, the freezing point is reduced by 0.99°C. Calculate the molar mass of the dissolved solute species and give its molecular formula.

* 77. The vapor pressure of an aqueous solution of $CaCl_2$ at 25°C is 0.02970 atm. The vapor pressure of pure water at the same temperature is 0.03126 atm. Estimate the freezing point of the solution.

78. Ethylene glycol (CH_2OHCH_2OH) is used in antifreeze because, when mixed with water, it lowers the freezing point below 0°C. What mass percentage of ethylene glycol in water must be used to reduce the freezing point of the mixture to −5.0°C, assuming ideal solution behavior?

79. A new compound has the empirical formula $GaCl_2$. This surprises some chemists who, based on the position of gallium in the periodic table, expect a chloride of gallium to have the formula $GaCl_3$ or possibly GaCl. They suggest that the "$GaCl_2$" is really $Ga[GaCl_4]$, in which the bracketed group behaves as a unit with a −1 charge. Suggest experiments to test this hypothesis.

* 80. Suppose two beakers are placed in a small closed container at 25°C. One contains 400 mL of a 0.100-M aqueous solution of NaCl; the second contains 200 mL of a 0.250-M aqueous solution of NaCl. Small amounts of water evaporate from both solutions. As time passes, the volume of

solution in the second beaker gradually increases, and that in the first gradually decreases. Why? If we wait long enough, what will the final volumes and concentrations be?

* **81.** The walls of erythrocytes (red blood cells) are permeable to water. In a salt solution, they shrivel (lose water) when the outside salt concentration is high and swell (take up water) when the outside salt concentration is low. In an experiment at 25°C, an aqueous solution of NaCl that has a freezing point of 0.406°C causes erythrocytes neither to swell nor to shrink, indicating that the osmotic pressure of their contents is equal to that of the NaCl solution. Calculate the osmotic pressure of the solution inside the erythrocytes under these conditions, assuming that its molarity and molality are equal.

82. Silver dissolves in molten lead. Compute the osmotic pressure of a 0.010 M solution of silver in lead at 423°C. Compute the height of a column of molten lead (ρ = 11.4 g cm^{-3}) to which this pressure corresponds.

83. Henry's law is important in environmental chemistry, where it predicts the distribution of pollutants between water and the atmosphere. Benzene (C_6H_6) emitted in wastewater streams, for example, can pass into the air, where it is degraded by processes induced by light from the sun. The Henry's law constant for benzene in water at 25°C is 301 atm. Calculate the partial pressure of benzene vapor in equilibrium with a solution of 2.0 g of benzene per 1000 L of water. How many benzene molecules are present in each cubic centimeter?

* **84.** Refer to the data of Problem 62. Calculate the mole fraction of toluene in a mixture of benzene and toluene that boils at 90°C under atmospheric pressure.

85. What is the difference between a solution and a colloidal suspension? Give examples of each, and show how, in some cases, it may be difficult to classify a mixture as one or the other.

CUMULATIVE PROBLEMS

86. A student prepares a solution by dissolving 1.000 mol of Na_2SO_4 in water. She accidentally leaves the container uncovered and comes back the next week to find only a white, solid residue. The mass of the residue is 322.2 g. Determine the chemical formula of this residue.

87. Complete combustion of 2.40 g of a compound of carbon, hydrogen, and oxygen yielded 5.46 g CO_2 and 2.23 g H_2O. When 8.69 g of the compound was dissolved in 281 g of water, the freezing point of the solution was found to be −0.97°C. What is the molecular formula of the compound?

* **88.** Imagine that two 1-L beakers, A and B, each containing an aqueous solution of fructose (a nonvolatile sugar with molecular weight = 180) are placed together in a box, which is then sealed. (The concentrations of the solutions are not necessarily the same.) The temperature remains constant at 26°C. Initially, there is 600 mL of solution in A and 100 mL of solution in B. As the solutions stand in the sealed box, their volumes change slowly for a while. When they stop changing, beaker A contains 400 mL and beaker B contains 300 mL. It is then determined that the solution in A is 1.5 M in fructose and has a density of 1.10 g mL^{-1}.

(a) What is the molar concentration of fructose in the solution in beaker B at the end? Explain.

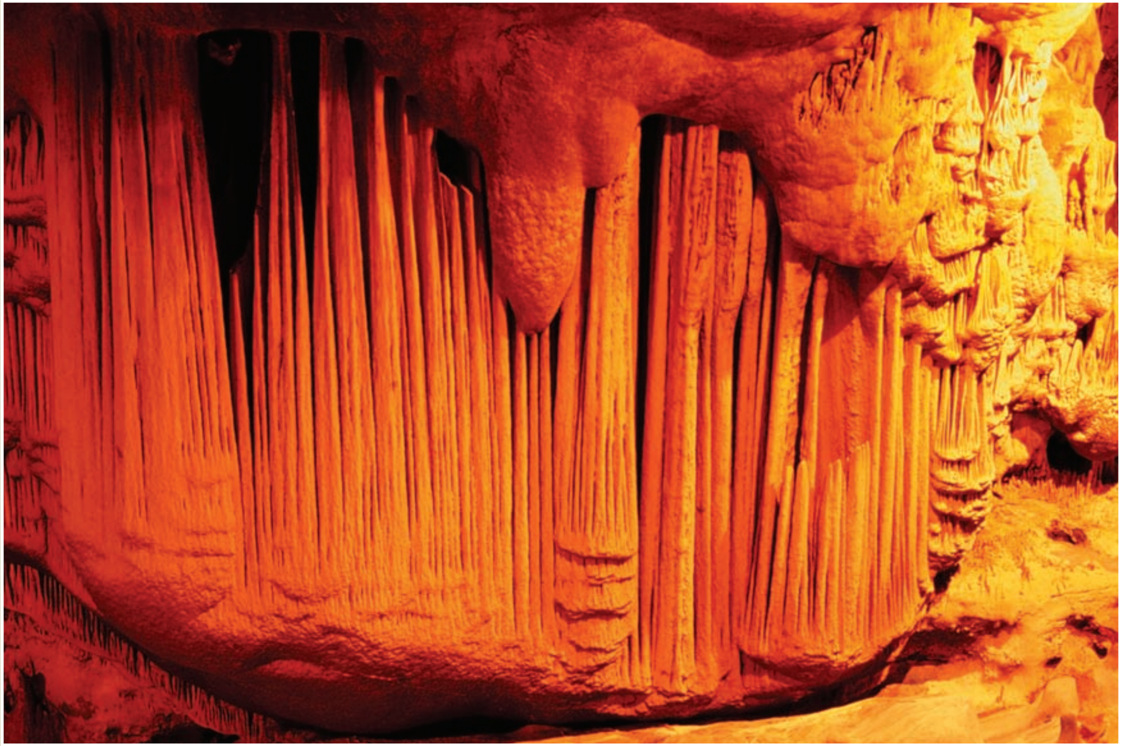
(b) Calculate the concentration of fructose in the solution in A at the start.

(c) Calculate the concentration of the fructose in the solution in B at the start.

(d) The vapor pressure of pure water at 26°C is 25.2 torr. What is the pressure of water vapor in the box at the end, after the volumes have stopped changing?

UNIT IV

Equilibrium in Chemical Reactions



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Stalactites (top) and stalagmites (bottom) consist of calcium carbonate. They form when a water solution containing Ca^{2+} and HCO_3^- ions enters a cave. Carbon dioxide is released, and calcium carbonate precipitates: $Ca^{2+}(aq) + 2\ HCO_3^-(aq) \longrightarrow CaCO_3(s) + H_2O + CO_2(g)$.

NOTE TO THE READER:
It is purely a matter of taste whether one should first study chemical equilibrium from the empirical point of view, and then study thermodynamics to provide the fundamental explanation of equilibrium, or learn thermodynamics first as essential background for the study of equilibrium. We have written this textbook to allow either approach. If your instructor prefers to cover thermodynamics before equilibrium, you should read Chapters 12, 13, and 14 straight through in the order written. If your instructor prefers to cover equilibrium from the empirical point of view before studying thermodynamics, you should skip now to Chapter 14 and omit those sections of Chapter 14 (clearly marked) that require background in thermodynamics. You should come back and read those sections later after you have studied Chapters 12 and 13.

How far do chemical reactions proceed toward completely consuming the reactants? What determines the extent of their progress? Experience shows that many reactions do not go to completion, but approach instead an *equilibrium state* in which products and unconsumed reactants are both present in specific, relative amounts. Once equilibrium has been achieved, the composition of the reaction mixture does not change any further. The equilibrium composition of the mixture is described quantitatively by the equilibrium constant for the reaction. If we know the equilibrium constant, we can calculate the equilibrium composition that will result from any initial composition. This is one of the most important tools available to chemists because it is used to predict and optimize the yield of reactions throughout fundamental and applied chemistry.

Heat influences the progress of chemical reactions—driving some forward while retarding others—and is quantitatively connected to chemical equilibrium by the science of thermodynamics. Thermodynamics predicts the equilibrium constant for a reaction from simple physical properties of the reactants and products and explains how the value of the equilibrium constant depends on the reaction temperature. In that way, thermodynamics shows how to increase the reaction yield by changing the reaction temperature.

UNIT CHAPTERS

CHAPTER 12
Thermodynamic Processes and Thermochemistry

CHAPTER 13
Spontaneous Processes and Thermodynamic Equilibrium

CHAPTER 14
Chemical Equilibrium

CHAPTER 15
Acid–Base Equilibria

CHAPTER 16
Solubility and Precipitation Equilibria

CHAPTER 17
Electrochemistry

UNIT GOALS

- To relate composition in the equilibrium state to the equilibrium constant
- To calculate composition in the equilibrium state from the equilibrium constant
- To describe the influence of temperature on the equilibrium constant
- To apply thermodynamics to explain these connections and optimize reaction yield

CHAPTER 12

Thermodynamic Processes and Thermochemistry

The steam locomotive operates by converting thermal energy into mechanical energy. The diesel locomotive converts chemical energy into electrical energy, then electrical energy into mechanical energy to generate motion. All these energy conversion processes are governed by thermodynamics. (a: ©DAJ/Getty Images; b: courtesy ©Kent Foster/Visuals Unlimited)

Experience shows that heat is the most important factor influencing the extent of chemical reactions. Heat drives some reactions toward completion, but retards the progress of others. Therefore, it is appropriate to launch our study of chemical equilibrium by learning how to measure the heat transfer in a chemical reaction. This objective leads us into the branch of physical science called thermodynamics, which describes the meaning of heat and gives procedures for measuring heat transfer quantitatively.

Thermodynamics is a broad and general subject with applications in all branches of the physical and biological sciences and engineering; thus, we limit our discussion to those aspects necessary for chemical equilibrium. In this chapter, we demonstrate that heat—which on first examination appears mysterious despite its familiarity—is just another form of energy, a form we call *thermal* energy. We describe how thermal energy is mutually convertible into mechanical and electrical energy, and how the total amount of energy is conserved during any such transfers. The previous sentence in more concise form is the first law of thermodynamics, which is the unifying theme of this chapter. We see how to measure quantitatively the heat transfer into a system through its *heat capacity.* We see how the transfer depends on experimental conditions such as constant pressure or constant volume. Finally, we apply these methods to measure the heat transfer in chemical reactions conducted at constant pressure. Then we are ready to connect heat transfer to chemical equilibrium at the beginning of Chapter 13.

We conclude this introduction with a general overview of thermodynamics, as context for the specific studies in this and the next chapter. Thermodynamics, in which a few apparently simple laws summarize a rich variety of observed behavior, is one of the surest and most powerful branches of science. The distinctive feature of thermodynamics is the universality of its basic laws, and the beauty of the subject is the many conclusions that can be deduced from those few laws. The laws of thermodynamics cannot themselves be derived or proved. Instead, they are generalizations drawn from a great many observations of the behavior of matter. The history of thermodynamics, like that of other fields of science, has been fraught with misconceptions. As we look back on the beginnings of the discipline in the 19th century, it appears to have developed with agonizing slowness. But it *has* developed, and its laws are the pillars on which much of modern science rests. The foundations of thermodynamics are completely understood today. It is being applied in research at the forefront of science, on systems ranging from black holes in distant parts of the universe to the growth and development of the biological cell. Many new results and insights are being acquired, but the foundations are not challenged.

Thermodynamics is an *operational* science, concerned with macroscopic, measurable properties and the relations among them. Its goal is to predict what types of chemical and physical processes are possible, and under what conditions, and to calculate quantitatively the properties of the equilibrium state that ensues when a process is conducted. For example, with thermodynamics we can answer the following types of chemical questions:

1. If hydrogen and nitrogen are mixed, is it possible for them to react? If so, what will be the percentage yield of ammonia?
2. How will a particular change in temperature or pressure affect the extent of the reaction?
3. How can the conditions for the reaction be optimized to maximize its yield?

Thermodynamics is an immensely practical subject. The knowledge from thermodynamics that a particular chemical process is impossible under certain proposed conditions can prevent great loss of time and resources spent vainly trying to conduct the reaction under those conditions. Thermodynamics can also suggest ways to change conditions so that a process becomes possible.

The power of thermodynamics lies in its generality: It rests on no particular model of the structure of matter. In fact, if the entire atomic theory of matter were to be found invalid and discarded (a *very* unlikely event!), the foundations of thermodynamics would remain unshaken. Nonetheless, thermodynamics has some important limitations. Thermodynamics asserts that substances have specific measurable macroscopic properties, but it cannot explain why a particular substance has particular numerical values for these properties. Thermodynamics can determine whether a process is possible, but it cannot say how rapidly the process will occur. For example, thermodynamics predicts that diamond is an unstable substance at atmospheric pressure and will eventually become graphite, but cannot predict how long this process will take.

12.1 Systems, States, and Processes

Thermodynamics uses abstract models to represent real-world systems and processes. These processes may appear in a rich variety of situations, including controlled laboratory conditions, industrial production facilities, living systems, the environment on Earth, and space. A key step in applying the methods of thermodynamics to such diverse processes is to formulate the thermodynamic model *for each process*. This step requires precise definitions of thermodynamic terms. Students (and professors!) of thermodynamics encounter—and sometimes create—apparent contradictions that arise from careless or inaccurate use of language. Part of the difficulty is that many thermodynamic terms also have everyday meanings different from their thermodynamic usage. This section provides a brief introduction to the language of thermodynamics.

A **system** is that part of the universe of immediate interest in a particular experiment or study. The system always contains a certain amount of matter and is described by specific parameters that are controlled in the experiment. For example, the gas confined in a closed box may constitute the system, characterized by the number of moles of the gas and the fixed volume of the box. But in other experiments, it would be more appropriate to consider the gas molecules in a particular cubic centimeter of space in the middle of a room to be the system. In the first case, the boundaries are physical walls, but in the second case, the boundaries are conceptual. We explain later that the two kinds of boundaries are treated the same way mathematically. In the second example, the system is characterized by its volume, which is definite, and by the number of moles of gas within it, which may fluctuate as the system exchanges molecules with the surrounding regions.

Systems are classified by the extent to which their boundaries permit exchange of matter and energy with the surrounding regions. In a **closed system,** the boundaries prevent the flow of matter into or out of it (the boundaries are **impermeable**), whereas the boundaries in an **open system** permit such flow. The amount of matter in an open system can change with time. An **isolated system** exchanges neither matter nor energy with the rest of the universe. **Rigid walls** prevent the system from gaining energy by mechanical processes such as compression and deformation; nonrigid walls permit mechanical energy transfer. **Adiabatic walls** prevent the system from gaining or losing thermal energy (described in detail later), whereas **diathermal walls** permit thermal energy transfer.

The definition of "the system" must be tailored to the specific process under consideration. Simple physical processes such as heating or cooling a metal object are modeled as closed systems (no matter is gained or lost) with diathermal (thermal energy is transferred) and nonrigid walls (the object may expand or contract). Most chemical reactions are modeled as open systems (matter is exchanged) with diathermal (thermal energy is transferred) and nonrigid walls (the density of the matter may change during the reaction). You will gain confidence in these classifications through experience as we examine many processes in this chapter.

The portion of the remainder of the universe that can exchange energy and matter with the system during the process of interest is called the **surroundings.** The surroundings provide the external forces that cause changes in the properties of the system during a process. The system and the surroundings together constitute the **thermodynamic universe** for that process. The thermodynamic universe for that process is isolated. Matter and energy are conserved in the thermodynamics universe while they are exchanged between the system and the surroundings during the process.

Thermodynamics is concerned with macroscopic properties of systems and changes in these properties during processes. Such properties are of two kinds: *extensive* and *intensive*. To distinguish between them, consider the following "thought experiment." Place a thin wall through the middle of a system, dividing it into two subsystems, each of which, like the system itself, is characterized by certain properties. An **extensive property** of the system can be written as the *sum* of the corresponding property in the two subsystems. Volume, mass, and energy are typical extensive properties; the volume of a system is the sum of the volumes of its subsystems. An **intensive property** of the system is the *same* as the corresponding property of each of the subsystems. Temperature and pressure are typical intensive properties; if a system at 298 K is divided in half, the temperature of each half will still be 298 K.

A **thermodynamic state** is a macroscopic condition of a system in which the properties of the system are held at selected fixed values independent of time. The properties of the system are held constant by its boundaries and the surroundings. For example, a system comprising 2 mol helium (He) gas can be held in a piston-cylinder apparatus that maintains the system pressure at 1.5 atm, and the apparatus may be immersed in a heat bath that maintains the system temperature at 298 K. The properties of pressure (P) and temperature (T) are then said to be **constrained** to the values 1 atm and 298 K, respectively. The piston-cylinder and the heat bath are the **constraints** that maintain the selected values of the properties P and T.

After the system has been prepared by establishing a set of constraints in the surroundings, after all disturbances caused by the preparation cease and none of its properties changes with time, the system is said to have reached **equilibrium.** The same equilibrium state can be reached from different directions. The thermodynamic state of a system comprising a given quantity of a liquid or gaseous pure substance is fixed when any two of its independent properties are given. Thus, the specification of P and T for 1 mol of a pure gas fixes not merely the volume, V, but all other properties of the material, such as the internal energy, U, which is defined in Section 12.2. These relations among properties can be displayed as three-dimensional plots of any property as a function of two other properties. For 1 mol of a gas, a plot of pressure against volume and temperature is shown in Figure 12.1. The resulting surface is represented by an equation giving P as a function of V and T; this is called the *equation of state* of the substance (see Section 9.7). If we avoid regions of small V and low T where gas nonideality becomes important, the experimentally determined surface is that shown in Figure 12.1, and the equation of state is given by the ideal gas law $PV = nRT$. The points on this surface (A, B, . . .) represent experimentally measured values of P in equilibrium thermodynamic states of the system fixed by particular values of V and T. Experience shows that the values of all other macroscopic properties take on definite values at each of these states. For example, we can visualize the internal energy, U, as a similar three-dimensional plot versus T and V.

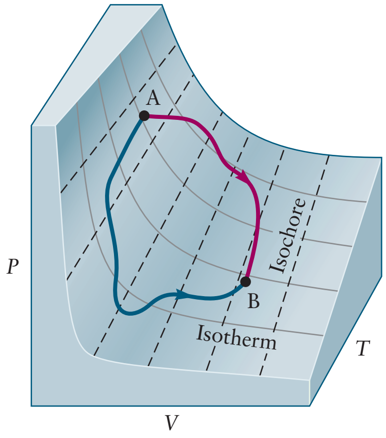

FIGURE 12.1 The *P*-*V*-*T* surface of 1 mol of ideal gas. Each point on the surface represents a combination of pressure (*P*), volume (*V*), and temperature (*T*) allowed by the equation of state of the gas. Along an isotherm (*T* constant), the pressure varies inversely with volume; along an isochore (*V* constant), it varies linearly with temperature. Two processes are shown connecting states A and B along paths that satisfy the equation of state at every point.

A **thermodynamic process** changes the thermodynamic state of a system. Such a process may be a *physical* (such as a change in the pressure of a gaseous system or the boiling of a liquid) or a *chemical* process, in which there is a change in the distribution of matter among different chemical species (for example, the reaction of solid $CaCO_3$, at 900 K and 1 atm pressure, to give solid CaO and gaseous CO_2 at the same temperature and pressure).

Because a process changes the state of a system, the process must start with the system in a particular equilibrium state and must also end with the system in a particular equilibrium state. Two such states A and B are indicated in Figure 12.1. You might wonder whether we can sketch a *path* on the surface of equilibrium thermodynamic states to summarize the progress of the system during a process. Only special processes of the type called *reversible* can be represented in this way (see discussion in the following paragraphs).

Many conditions of a system do not correspond to any equilibrium thermodynamic state. Suppose a gas is confined by a piston in a cylinder with volume V_1

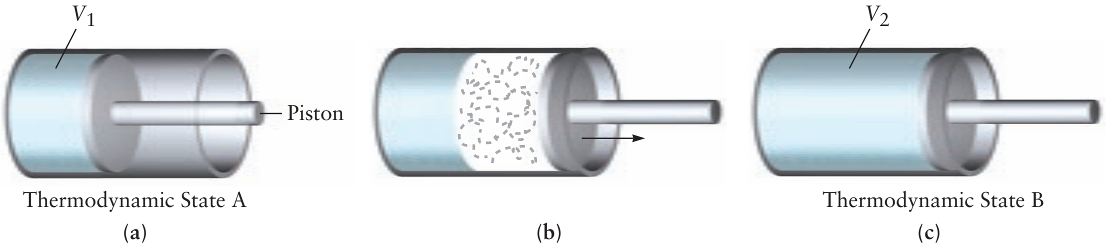

FIGURE 12.2 Stages in an irreversible expansion of a gas from an initial state (a) of volume V_1 to a final state (c) of volume V_2. In the intermediate stage shown (b), the gas is not in equilibrium; because of turbulence, pressure and temperature cannot be defined.

(thermodynamic state A). If the piston is abruptly pulled out to increase the volume to V_2 (Fig. 12.2), chaotic gas currents arise as the molecules begin to move into the larger volume. These intermediate stages are not thermodynamic states, because such properties as density and temperature are changing rapidly through space and in time. Eventually, the currents cease and the system approaches a new equilibrium thermodynamic state, B. States A and B are thermodynamic states, but the conditions in between cannot be described by only a few macroscopic variables, and therefore are not thermodynamic states. Such a process is called **irreversible.** An irreversible process cannot be represented as a path on a thermodynamic surface (as in Fig.12.1), because the intermediate stages are not thermodynamic equilibrium states and thus do not correspond to points on the equation-of-state surface.

In contrast, a **reversible process** proceeds through a continuous series of thermodynamic states, and thus can be shown as a path on the equation-of-state surface. Such a process is an idealization, because the final equilibrium state would be reached only after an infinite length of time; therefore, such a process could never occur in a finite time. If a real process is conducted slowly enough and in sufficiently small steps, the real (irreversible) process can be approximated by the idealized limiting reversible process. The term *reversible* is used because an infinitesimal change in external conditions suffices to reverse the direction of motion of the system. For example, if a gas is expanded by slowly pulling out a piston, only a tiny change in the forces exerted from the outside is required to change the direction of motion of the piston and begin to compress the gas. A gas confined inside a piston-cylinder arrangement will experience an irreversible compression when a kilogram of sand is suddenly dropped onto the piston. The same compression can be achieved (almost) reversibly by transferring the same kilogram of sand onto the piston one grain at the time.

An infinite number of reversible paths can be identified between any two thermodynamic states A and B. Two of them shown in Figure 12.1 could be realized by slowly changing the values of T and V in the proper sequence by manipulating the apparatus in the surroundings. We use such reversible paths throughout this textbook as a tool for calculating changes in properties caused by processes.

Certain properties of a system, called **state functions,** are uniquely determined by the thermodynamic state of the system. Volume, temperature, pressure, and the internal energy, U, are examples of state functions. The Greek letter delta (Δ) is used to indicate *changes* in state functions in a thermodynamic process. Thus, $\Delta V = V_{\text{final}} - V_{\text{initial}}$ (or $V_f - V_i$) is the change in volume between initial and final states, and $\Delta U = U_{\text{final}} - U_{\text{initial}}$ is the corresponding change in internal energy. Because ΔU (or ΔV or ΔT) depends only on the initial and final states, the same change, ΔU, will be measured no matter which path (reversible or irreversible) is followed between any given pair of thermodynamic states. *The change in any state function between two states is independent of path.* The converse statement is also true: If the change in a property of a system is independent of path, the property is a state function. Figure 12.3 illustrates two different paths that connect a given initial state and a common final state.

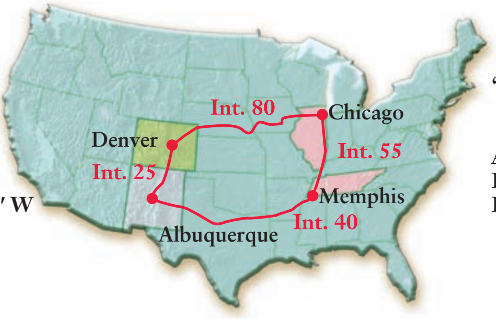

FIGURE 12.3 Differences in state properties (such as the difference in altitude between two points) are independent of the path followed. Other properties (such as the total distance traveled) depend on the particular path.

"State Properties"
of Denver:

Altitude 1 mile
Latitude 39° 43′ N
Longitude 105° 01′ W

"State Properties"
of Chicago:

Altitude 656 ft.
Latitude 41° 51′ N
Longitude 87° 38′ W

Path values
(distances between Chicago and Denver):
996 miles via Int. 80
1957 miles via Memphis and Albuquerque
on Int. 55, Int. 40, and Int. 25

State property
differences:
Δ (altitude) = 5280 – 656 = 4624 ft.
Δ (latitude) = 39° 43′ – 41° 51′ = –2° 8′
Δ (longitude) = 105° 01′ – 87° 38′ = 17° 23′

12.2 The First Law of Thermodynamics: Internal Energy, Work, and Heat

The first law of thermodynamics (which is stated at the end of this section) relates the energy change in a thermodynamic process to the amount of work done on the system and the amount of heat transferred to the system. It is first necessary to examine the ways in which amounts of heat and work are measured to understand the significance of this law. You will see that heat and work are simply different means by which energy is transferred into or out of a system.

Work

The mechanical definition of **work** is the product of the external force on a body times the distance through which the force acts. If a body moves in a straight line from point r_i to r_f with a constant force, F, applied along the direction of the path, the work done on the body is

$$w = F(r_f - r_i) \qquad \text{(force along direction of path)}$$

To illustrate how work can change the energy of a system, we will examine the relation between work and energy in an ordinary mechanical system.

As the first example, consider a block of mass, M, moving with initial velocity v_i along a frictionless surface. We know that a force acting on an object increases the velocity, and therefore the kinetic energy of the object. In the following derivation, we show how the kinetic energy of an object changes when work is done on it. If a constant force, F, is exerted on it in the direction of its motion, it will experience a constant acceleration, $a = F/M$. After a time, t, the velocity of the block will have increased from v_i to v_f, and its position will have changed from r_i to r_f. The work done on the block is

$$w = F(r_f - r_i) = Ma(r_f - r_i)$$

The distance traveled, $r_f - r_i$, is given by the average velocity, in this case $(v_i + v_f)/2$, multiplied by the elapsed time, t:

$$r_f - r_i = \left(\frac{v_i + v_f}{2}\right)t$$

When the acceleration is constant, it is equal to the change in velocity, $v_f - v_i$, divided by the elapsed time:

$$a = (v_f - v_i)/t$$

Substituting both of these results into the expression for the work done gives

$$\begin{aligned} w &= M\left(\frac{v_f - v_i}{t}\right)\left(\frac{v_i - v_f}{2}\right)t \\ &= \frac{M}{2}(v_f - v_i)(v_f + v_i) \\ &= \frac{M}{2}v_f^2 - \frac{M}{2}v_i^2 \\ &= \Delta E_{kin} \end{aligned}$$

The expression on the right side of the equations is the change in kinetic energy, $\frac{1}{2}Mv^2$, of the block. For this idealized example with a frictionless surface, the work done is equal to the change in energy (in this case, kinetic) of the block.

As a second mechanical example, consider the work done in lifting an object in a gravitational field. To raise a mass, M, from an initial height, h_i, to a final height, h_f, an upward force sufficient to counteract the downward force of gravity, Mg, must be exerted. The work done on the object in this case is

$$w = Mg(h_f - h_i) = Mg\Delta h = \Delta E_{pot}$$

This is the change in *potential* energy, Mgh, of the object, showing once again a connection between mechanical work done and a change in energy.

One important kind of mechanical work in chemistry is **pressure–volume work,** which results when a system is compressed or expanded under the influence of an outside pressure. Imagine that a gas has pressure P_i and is confined in a cylinder by a frictionless piston of cross-sectional area A and negligible mass (Fig. 12.4). The force exerted on the inside face of the piston by the gas is $F_i = P_iA$, because pressure is defined as force divided by area. If there is a gas on the outer side of the piston with pressure P_{ext} ("ext" for "external"), then if $P_{ext} = P_i$, the piston will experience no net force. If P_{ext} is increased, the gas will be compressed, and if it is decreased, the gas will expand. Consider first the case in which the external force is less than the initial force exerted by the gas, P_iA. Then the gas will expand and lift the piston from h_i to h_f. The work in this case is

$$w = -F_{ext}(h_f - h_i)$$

The negative sign is inserted because the force from the gas outside opposes the direction of displacement of the piston during expansion of the gas inside the cylinder. This is rewritten as

$$w = -P_{ext}A\Delta h$$

The product $A\Delta h$ is the volume change of the system, ΔV, so the work is

$$w = -P_{ext}\,\Delta V \qquad [12.1]$$

For an expansion, $\Delta V > 0$, thus $w < 0$ and the system does work; it pushes back the surroundings. For a compression (by making $P_{ext} > P_i$), work is done *on* the system; it is pushed back by the surroundings. Again, $w = -P_{ext}\Delta V$, but now $\Delta V < 0$, so $w > 0$. If there is no volume change, $\Delta V = 0$, and no pressure–volume work is done. Finally, if there is no mechanical link to the surroundings (that is, if $P_{ext} = 0$), then once again no pressure–volume work can be performed because the volume is not changed.

If the pressure P_{ext} is expressed in pascals and the volume in cubic meters, their product is in joules (J). These are the International System of Units (SI) units for

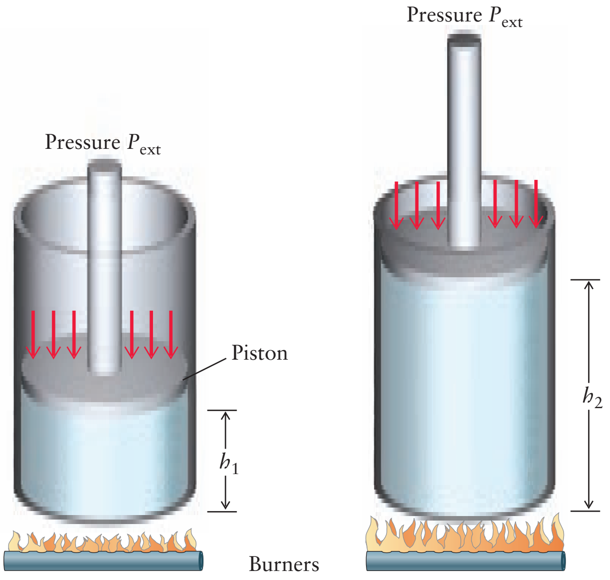

FIGURE 12.4 As the gas inside this cylinder is heated, it expands, pushing the piston against the pressure P_{ext} exerted by the gas outside. As the piston is displaced over a distance $h_f - \Delta h_i = \Delta h$, the volume of the cylinder increases by an amount $A\,\Delta h$, where A is the surface area of the piston.

these quantities. For many purposes, it is more convenient to express pressures in atmospheres and volumes in liters; therefore, work has the unit liter-atmospheres (L atm). The two work units are related by

$$1 \text{ L atm} = (10^{-3} \text{ m}^3)(1.01325 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2}) = 101.325 \text{ J}$$

EXAMPLE 12.1

A cylinder confines 2.00 L gas under a pressure of 1.00 atm. The external pressure is also 1.00 atm. The gas is heated slowly, with the piston sliding freely to maintain the pressure of the gas close to 1.00 atm. Suppose the heating continues until a final volume of 3.50 L is reached. Calculate the work done on the gas and express it in joules.

SOLUTION

This is an expansion of a system from 2.00 to 3.50 L against a constant external pressure of 1.00 atm. The work done on the system is then

$$w = -P_{ext}\,\Delta V = -\,(1.00 \text{ atm})(3.50 \text{ L} - 2.00 \text{ L}) = -1.50 \text{ L atm}$$

Conversion to joules gives

$$w = (-1.50 \text{ L atm})(101.325 \text{ J L}^{-1} \text{ atm}^{-1}) = -152 \text{ J}$$

Because w is negative, we see that −152 J of work was done *on* the gas. Put another way, +152 J of work was done *by* the gas as it expanded against atmospheric pressure.

Related Problems: 1, 2

Internal Energy

In the two simple mechanical cases discussed earlier, we saw how performing work changes the amount of two types of energy: the kinetic energy of a moving object and the potential energy of an object in a gravitational field. In the same way, performing work can change the amount of energy in more complex cases. A third type of energy, less apparent but equally important, is **internal energy,** defined as the total energy content of a system arising from the potential energy between molecules, from the kinetic energy of molecular motions, and from chemical energy stored in chemical bonds. Potential energy between molecules includes the lattice energy of solids and the attractive and repulsive interactions between molecules in gases and liquids. Kinetic energy appears in the translation and the internal motions of individual molecules (Fig. 12.5). Gas molecules are in a constant state of motion (see Section 9.5) even when no overall gas flow is taking place in the container; the same is true of molecules in liquids and solids. Example 12.1 illustrates how performing work can change the internal energy of a system. In this example, the system reduced its internal energy by performing +152 J of work against the surroundings. Had the gas been compressed instead of expanding, the internal energy of the system would have increased by the amount of work done on it. *We conclude that P-V work is a means of changing the internal energy of a macroscopic system through purely mechanical interaction between the system and its surroundings.*

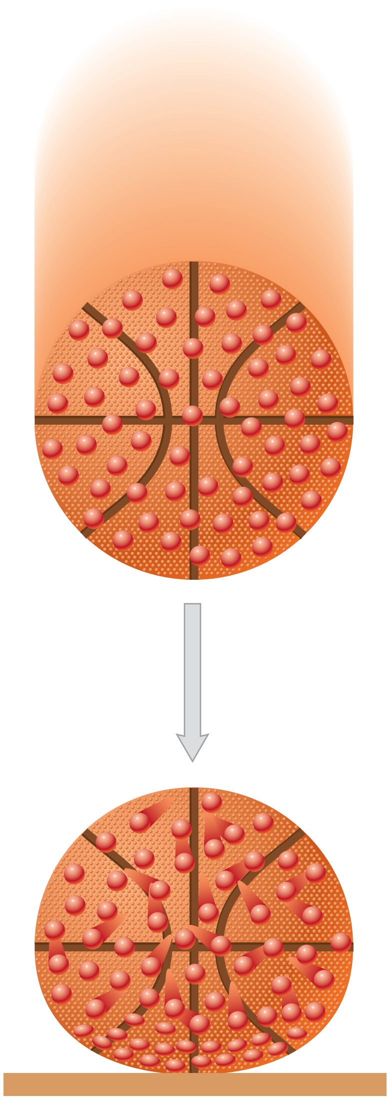

FIGURE 12.5 A ball dropped from a height increases its internal energy on impact with the ground. After impact, the molecules near the surface of the ball are pushed against one another, increasing the potential energy between the molecules. As the ball bounces, the molecules readjust their positions, after which they move a little faster. The kinetic energy of the molecules is higher than it was just before impact with the ground.

Heat

Now, how do we describe the role of heat in the process in Example 12.1? After all, heating the gas caused it to expand, which enabled it to move the piston and do work on the surroundings. The heater in Figure 12.4 has no mechanical "moving parts," yet it set in motion a train of events that led to a mechanical result. To explain this result, we interpret *heat as a means of increasing the internal energy of a system without mechanical interaction.* Justification for this procedure is provided later in this chapter.

The amount of energy transferred between two objects initially at different temperatures is called **heat,** or **thermal energy.** When a hot body is brought into contact with a colder body, the two temperatures change until they become equal. If a piece of hot metal is plunged into a container of water, the temperature of the water increases as its molecules begin to move faster, corresponding to an increase in the internal energy of the water. This process is sometimes described as the "flow" of heat from the hotter to the colder body. Although this picture is useful, it is based on the antiquated (and erroneous) notion that heat is a sort of fluid contained in matter.

The idea of heat flow has inspired methods for measuring the amount of energy transferred as heat; this branch of science is called **calorimetry.** One simple way is to use an **ice calorimeter** (Fig. 12.6), which consists of a bath containing ice and water, well insulated to prevent heat transfer to the surroundings. If heat is transferred to the bath from the system, some of the ice melts. Because a given mass of water has a smaller volume than the same mass of ice, the total volume of the ice–water mixture decreases as heat enters the bath. If twice as much heat is transferred, twice as much ice will melt and the volume change will be twice as great. The amount of heat transferred is determined from the change in volume of the contents of the calorimeter. Heat transferred from the ice bath *into* the system causes water to freeze and *increases* the total volume of the ice bath.

More contemporary versions of calorimetry use the fact that when heat is transferred to or removed from a substance in a single phase at constant pressure, the temperature changes in a reproducible way. The **specific heat capacity** of a material is the amount of heat required to increase the temperature of a 1-g mass by 1°C. If twice as much heat is transferred, the resulting temperature change will be twice as large (provided the specific heat capacity itself does not change appreciably with temperature). Thus, the temperature change of a fixed amount of a given substance is a measure of the thermal energy transferred to or from it. This is described by

$$q = Mc_s\Delta T \qquad [12.2]$$

where q is the heat transferred to a body of mass M with specific heat capacity c_s to cause a temperature change of ΔT.

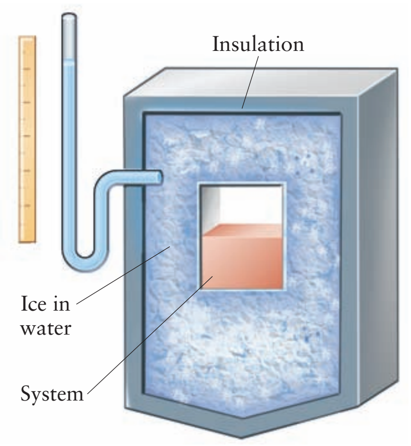

FIGURE 12.6 An ice calorimeter. As the ice melts, the volume of the ice–water mixture decreases, an effect that can be read off the scale on the left.

Because heat, like work, is a form in which energy is transferred, the appropriate unit for it is also the joule. Historically, however, the connections among work, heat, and energy were not appreciated until the middle of the 19th century, by which time a separate unit for heat, the calorie, was already well established. One calorie was defined as the amount of heat required to increase the temperature of 1 g water from 14.5°C to 15.5°C (or, in other words, the specific heat capacity of water, c_s, at 15°C was *defined* as 1.00 cal K^{-1} g^{-1}).

The equivalence of heat and work as means of energy transfer was suggested in 1798 by Benjamin Thompson, Count Rumford. In the course of his work as military advisor to the King of Bavaria, Thompson observed that the quantity of heat produced in boring cannons was proportional to the amount of work done in the process. Moreover, the operation could be continued indefinitely, demonstrating that heat was not a "fluid" contained in the metal of the cannon. More quantitative measurements were conducted by the German physician Julius Mayer and by the English physicist James Joule. In the 1840s, these scientists showed that the temperature of a substance could be increased by doing work on the substance, as well as by adding heat to it. Figure 12.7 shows an apparatus in which a paddle, driven by a falling weight, churns the water in a tank. Work is performed on the water, and the temperature increases. The work done is $-Mg\,\Delta h$, where Δh is the (negative) change in the height of the weight and M is its mass. The experiment is conducted in an insulated container, so no heat enters the container or leaks out to the surroundings. Because all this work goes to increase the water temperature, the specific heat capacity of the water in *joules* per gram per degree is equal to the quantity of work done divided by the product of the mass of water and its temperature increase.

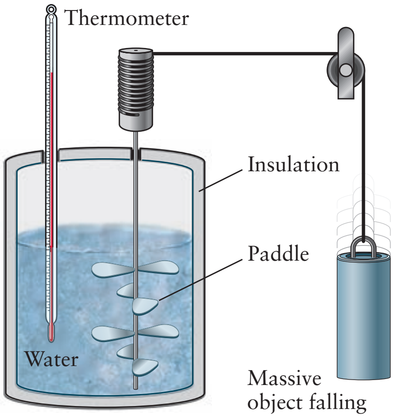

FIGURE 12.7 The falling weight turns a paddle that does work on the system (the water), causing an increase in its temperature.

EXAMPLE 12.2

Suppose a 10.00-kg mass drops through a height difference of 3.00 m, and the resulting work is used to turn a paddle in 200.0 g water, initially at 15.00°C. The final water temperature is found to be 15.35°C. Assuming that the work done is used entirely to increase the water temperature, calculate the conversion factor between joules and calories.

SOLUTION

The total work done is

$$w = -Mg\Delta h = -(10.00\text{ kg})(9.807\text{ m s}^{-2})(-3.00\text{ m}) = 294\text{ J}$$

The heat (in calories) required to increase the water temperature by the same amount is

$$q = Mc_s\Delta T = (200.0\text{ g})(1.000\text{ cal K}^{-1}\text{ g}^{-1})(0.35\text{ K}) = 70\text{ cal}$$

Because the work done has the same effect on the water as direct transfer of heat, these two expressions can be set equal to each other, giving

$$70\text{ calories} = 294\text{ joules}$$

$$1\text{ calorie} \approx 4.2\text{ joules}$$

Related Problems: 3, 4

These and other experiments eliminated the need for the calorie as an independent unit, and the calorie is now *defined* as

$$1\text{ cal} = 4.184\text{ J} \quad (\text{exactly})$$

This book uses the joule as the primary unit for heat and energy. Because much of the chemical literature continues to use the calorie as the unit of heat, it is important to be familiar with both units.

The First Law of Thermodynamics

Both heat and work are forms in which energy is transferred into and out of a system; they can be thought of as energy in transit. If the energy change is caused by *mechanical* contact of the system with its surroundings, work is done; if it is caused by *thermal* contact (leading to equalization of temperatures), heat is transferred. In many processes, both heat and work cross the boundary of a system, and the change in the internal energy, U, is the sum of the two contributions. We denote the internal energy by U to distinguish it from the sum of the potential and kinetic energy in a simple mechanical process, for which we use the symbol E throughout this book. This statement, called the **first law of thermodynamics,** takes the mathematical form[1]

$$\boxed{\Delta U = q + w} \qquad [12.3]$$

A system cannot be said to "contain" work or heat, because both "work" and "heat" refer not to states of the system but to *processes* that transform one state into another. In the Joule experiment shown in Figure 12.7, the work done on the water (the system) by the falling weight increased the temperature of the water. Work was performed on the system, and no heat was transferred; thus, the first law for this process takes the form $\Delta U = w$. The same change in state of the system can be achieved by transferring heat to the system without work being done; for this process, $\Delta U = q$. Because q and w depend on the particular process (or path) connecting the states, they are not state functions. But their sum, $\Delta U = q + w$, is independent of path; therefore, internal energy is a function of state. The fundamental physical content of the first law of thermodynamics is the following observation:

> *Although q and w depend individually on the path followed between a given pair of states, their sum ΔU does not.*

We stated earlier that the laws of thermodynamics cannot be derived or proved; they are generalizations of the results of countless experiments on a tremendous variety of substances. It is not possible even to "check" the first law by independently measuring ΔU, w, and q, because no "energy gauges" exist to determine energy changes ΔU. But what we *can* do is to measure w and q for a series of different processes connecting the same initial and final states. Every time, we find that their sum, $q + w$, is always the same.

In any process, the heat *added to* the system is *removed from* the surroundings; thus,

$$q_{\text{sys}} = -q_{\text{surr}}$$

In the same way, the work done *on* the system is done *by* the surroundings; thus,

$$w_{\text{sys}} = -w_{\text{surr}}$$

Adding these two and invoking the first law give

$$\Delta U_{\text{sys}} = -\Delta U_{\text{surr}}$$

---

[1] Some books, especially older ones, define work as positive when it is done *by* the system. The reason is that many engineering applications focus on the work done by a particular heat engine; therefore, it is helpful to define that quantity as positive. Thus, the work is given by

$$w = P_{\text{ext}}\,\Delta V \text{ (older convention)}$$

and the first law reads

$$\Delta U = q - w \text{ (older convention)}$$

Although we do not use the older convention, you should check which convention is used when consulting other books.

Thus, the energy changes of system and surroundings have the same magnitude but opposite signs. The total energy change of the thermodynamic universe for a given process (system plus surroundings) is then

$$\Delta U_{\text{univ}} = \Delta U_{\text{sys}} + \Delta U_{\text{surr}} = 0 \qquad [12.4]$$

Our conclusion is that, in any process, the total energy of the thermodynamic universe remains unchanged; the total energy is conserved while it is exchanged between the system and the surroundings. This is another way to state the first law of thermodynamics.

12.3 Heat Capacity, Enthalpy, and Calorimetry

Section 12.2 defines specific heat capacity as the amount of heat required to increase the temperature of 1 g of material by 1 K. That definition is somewhat imprecise, because, in fact, the amount of heat required depends on whether the process is conducted at constant volume or at constant pressure. This section describes precise methods for measuring the amount of energy transferred as heat during a process and for relating this amount to the thermodynamic properties of the system under investigation.

Heat Capacity and Specific Heat Capacity

The **heat capacity, C,** is defined as the amount of energy that must be added to the system to increase its temperature by 1 K. The heat capacity is a property of the system as a whole and has units of J K^{-1}.

$$q = C\Delta T$$

Now consider a case in which two gaseous systems containing identical masses of the same substance are heated to produce identical changes in temperature. During the experiment, system 1 is held at constant volume, and system 2 at constant pressure. Which system absorbed more heat in these identical temperature changes? All the energy gained by system 1 contributed to increasing the temperature of the substance, and therefore the speed of the molecules, subject to the fixed volume. But in system 2, some of the energy gained was promptly lost as the system performed expansion work against the surroundings at constant pressure. Consequently, system 2 must absorb more thermal energy from the surroundings than does system 1 to achieve the identical temperature change. Two independent heat capacity functions must be defined: C_P, the heat capacity at constant pressure, and C_V, the heat capacity at constant volume. For any system, C_P is greater than C_V. This difference can be quite large for gases. It is usually negligible for solids and liquids, because their only volume change at constant pressure is the small expansion or contraction on heating and cooling.

In thermodynamics, the *molar* heat capacities c_V and c_P (the system heat capacities C_V and C_P divided by the number of moles of substance in the system) are particularly useful: c_V is the amount of heat required to increase the temperature of 1 mol of substance by 1 K at constant volume, and c_P is the corresponding amount required at constant pressure. If the total heat transferred to n moles at constant volume is q_V, then

$$q_V = nc_V(T_2 - T_1) = nc_V\Delta T \qquad [12.5]$$

TABLE 12.1 Specific Heat Capacities at Constant Pressure (at 25°C)

Substance	Specific Heat Capacity (J K^{-1} g^{-1})
$Hg(\ell)$	0.140
$Cu(s)$	0.385
$Fe(s)$	0.449
$SiO_2(s)$	0.739
$CaCO_3(s)$	0.818
$O_2(g)$	0.917
$H_2O(\ell)$	4.18

If an amount q_P is transferred at constant pressure, then

$$q_P = nc_P\Delta T \qquad [12.6]$$

provided that c_V and c_P do not change significantly between the initial and final temperatures. The *specific heat capacity* at constant V or constant P is the system heat capacity reported per gram of substance. Extensive tabulations of the molar and specific heat capacities are available. Representative values are listed in Table 12.1. We give a molecular interpretation of heat capacity for ideal gases in Section 12.4.

When two objects at different temperatures are brought into contact, energy in the form of heat is exchanged between them until they reach a common temperature. If the two objects together are insulated from their surroundings, the amount of heat q_2 taken up by the cooler object is equal to $-q_1$, the amount of heat given up by the hotter object. As always, the convention followed is that energy transferred to an object has a positive sign; thus, q_2 is positive when q_1 is negative. This analysis is broadly applicable; a typical example follows.

EXAMPLE 12.3

A piece of iron weighing 72.4 g is heated to 100.0°C and plunged into 100.0 g water that is initially at 10.0°C in a Styrofoam cup calorimeter. Assume no heat is lost to the Styrofoam cup or to the environment (Fig. 12.8). Calculate the final temperature that is reached.

SOLUTION

The "coffee cup calorimeter" operates at constant pressure determined by the atmosphere; therefore, we need specific heat data at constant pressure. Because the data involve masses, it is easier to work with specific heat capacities (see Table 12.1) than with molar heat capacities. If t_f is the final temperature (in degrees Celsius), then the equation for heat balance gives

$$M_1(c_{s1})\Delta T_1 = -M_2(c_{s2})\Delta T_2$$

$$(100.0 \text{ g } H_2O)(4.18 \text{ J °C}^{-1} \text{ g}^{-1})(t_f - 10.0°C) =$$
$$-(72.4 \text{ g Fe})(0.449 \text{ J°C}^{-1} \text{ g}^{-1})(t_f - 100.0°C)$$

This is a linear equation for the unknown temperature t_f, and its solution is

$$418t_f - 4180 = -32.51t_f + 3251$$

$$t_f = 16.5°C$$

Note that specific heat capacities are numerically the same whether expressed in J K^{-1} g^{-1} or J $(°C)^{-1}$ g^{-1} (because the degree Celsius and the kelvin have the same size). Converting 10.0°C and 100.0°C to kelvins and using specific heat capacities in units of J K^{-1} g^{-1} gives t_f = 289.7 K, which is equivalent to the previous answer.

Related Problems: 11, 12

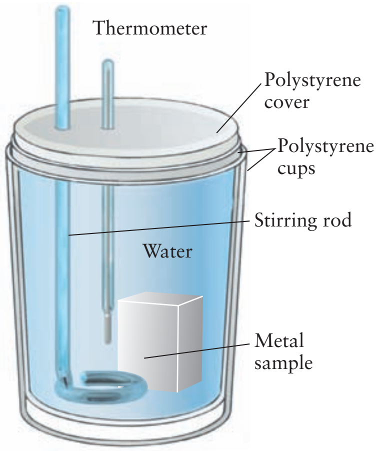

FIGURE 12.8 A Styrofoam cup calorimeter. As the piece of metal cools, it releases heat to the water. The amount of heat released can be determined from the temperature change of the water. The hot metal is the "system"; the water is the "surroundings." The Styrofoam cup wall prevents energy exchange with the remainder of the room and is the boundary of the "thermodynamic universe" for this problem.

Heat Transfer at Constant Volume: Bomb Calorimeters

Suppose some reacting species are sealed in a small closed container (called a *bomb*) and the container is placed in a calorimeter like the one in Figure 12.9. The reaction is initiated by a heated wire inside the bomb. As the molecules react chemically, heat is given off or taken up, and the change in temperature of the calorimetric fluid is measured. Because the container is sealed tightly, its volume is

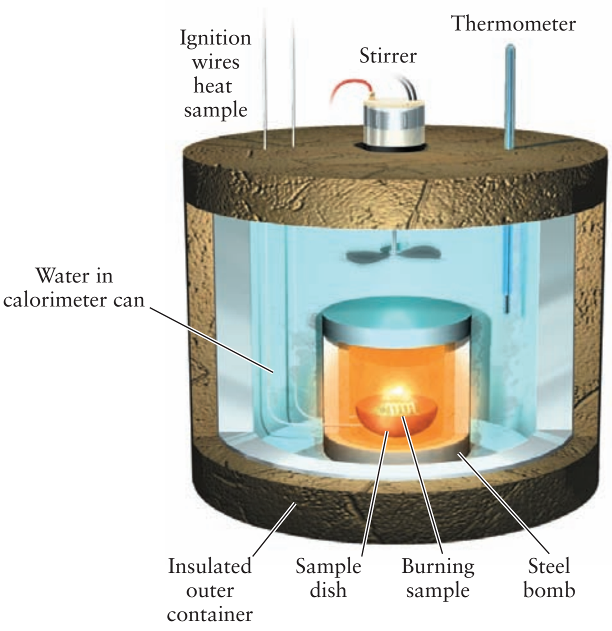

FIGURE 12.9 The combustion calorimeter is also called a "bomb calorimeter"; the combustion reaction in it is conducted at a fixed volume.

constant and no pressure–volume work is done. Therefore, the change in internal energy is equal to the measured heat absorbed from the chemical reaction at constant volume:

$$\Delta U = q_V$$

Such experiments at constant volume are often inconvenient or difficult to perform. They require the use of a well-constructed reaction vessel that can resist the large pressure changes that occur in many chemical reactions.

Heat Transfer at Constant Pressure: Enthalpy

Most chemical reactions are done under constant (atmospheric) *pressure* conditions rather than at constant volume, so it is desirable to relate the heat transferred at constant pressure, q_P, to some state property analogous to the internal energy, U.

If the work done is entirely pressure–volume work, and if the external pressure is held constant, then

$$\Delta U = q_P + w = q_P - P_{ext}\Delta V$$

If the external pressure is now assumed to be equal to the internal pressure of the system P, then

$$\Delta U = q_P - P\Delta V$$

$$q_P = \Delta U + P\Delta V$$

Because P is constant, $P\Delta V = \Delta(PV)$, and this equation becomes

$$q_P = \Delta(U + PV)$$

The combination $U + PV$ appearing on the right side is now defined as the **enthalpy** H:

$$\boxed{H = U + PV} \qquad [12.7a]$$

thus,

$$q_P = \Delta(U + PV) = \Delta H \qquad [12.7b]$$

Because U, P, and V are state functions, H must also be a state function. Heat transfer in a process at constant pressure has therefore been related to the change in a state function.

It is important to remember that

$$\Delta H = q_P = \Delta U + P\Delta V \qquad \text{(constant pressure)}$$

holds only at constant pressure. If the pressure changes, the more general relationship

$$\Delta H = \Delta U + \Delta(PV)$$

must be used. Like the energy, the enthalpy change is determined by the initial and final states and is independent of the particular path along which the process is performed. This is always true for a state function.

Physical interpretation of the enthalpy function follows immediately from the equation $\Delta H = \Delta U + P\Delta V$ at constant pressure. Clearly, H has physical dimensions of energy and is, in effect, a "corrected" internal energy that reflects the consequences of changing V while thermal energy is being absorbed at constant pressure. The "correction term" $P\Delta V$ accounts precisely for the energy used in expansion work, rather than for increasing the temperature of the system. Thus, the value of q in constant pressure processes where only pressure–volume work is done is equivalent to the change in the state function enthalpy, ΔH.

12.4 Illustrations of the First Law of Thermodynamics in Ideal Gas Processes

We stated the first law of thermodynamics in a general form, applicable to any process that begins and ends in equilibrium states. We analyzed the heat and work terms separately and presented methods for calculating, measuring, and interpreting each. All the concepts are now in place for applying thermodynamics to the discussion of specific processes. Applications require data on certain properties of the substance being studied, such as its equation of state and its heat capacities. Thermodynamic arguments alone cannot provide the actual values of such properties; instead, thermodynamics establishes universal relations among such properties. The actual values must be obtained by methods other than thermodynamics, such as experimental measurements or theoretical calculations in statistical thermodynamics. To illustrate these points, in the next few paragraphs we obtain data on the heat capacities of ideal gases by methods outside thermodynamics. Then we use these data to apply thermodynamics to analyze particular processes carried out on ideal gases.

Heat Capacities of Ideal Gases

The pair of molar heat capacities c_V and c_P for an ideal monatomic gas can be calculated from the results of the kinetic theory of gases and the ideal gas equation of state. From Section 9.5, the average translational kinetic energy of n moles of an ideal gas is

$$E_{\text{kin}} = \tfrac{3}{2}\, nRT$$

As shown in Chapter 17, the rotations and vibrations of diatomic or polyatomic molecules make additional contributions to the energy. In a *monatomic* gas, these other contributions are not present; thus, changes in the total internal energy ΔU measured in thermodynamics can be equated to changes in the translational kinetic energy of the atoms. If n moles of a monatomic gas is taken from a temperature T_1 to a temperature T_2, the internal energy change is

$$\Delta U = \tfrac{3}{2}\,nR(T_2 - T_1) = \tfrac{3}{2}\,nR\Delta T$$

Note that the pressure and volume do not affect U explicitly (except through temperature changes), so this result is independent of the change in pressure or volume of the gas.

Now, consider changing the temperature of an ideal gas at constant volume from the point of view of thermodynamics. Because the volume is constant (the gas is confined in a vessel with rigid, diathermal walls), the pressure–volume work, w, must be zero; therefore,

$$\Delta U = q_V = nc_V\Delta T \qquad \text{(ideal gas)}$$

where q_V is the heat transferred at constant volume. Equating this thermodynamic relation with the previous expression for ΔU (from kinetic theory) shows that

$$c_V = \tfrac{3}{2}\,R \qquad \text{(monatomic ideal gas)} \qquad [12.8]$$

Similarly, the molar heat capacity at constant pressure, c_P, is calculated by examining the heating of a monatomic ideal gas at constant pressure from temperature T_1 to T_2. Experimentally, such a process can be performed by placing the gas in a cylinder with a piston that moves out as the gas is heated, keeping the gas pressure equal to the outside pressure. In this case,

$$\Delta U = \tfrac{3}{2}\,nR\Delta T = nc_V\Delta T$$

still holds (because the energy change depends only on the temperatures for an ideal gas), but we now have

$$\Delta U = q_P + w$$

because the work is no longer zero. The work for a constant-pressure process is easily calculated from

$$w = -P\Delta V = -P(V_2 - V_1)$$

and the heat transferred is

$$q_P = nc_P\Delta T$$

Because w is negative, q_P is larger than q_V by the amount of work done by the gas as it expands. This gives

$$\Delta U = q + w$$

$$nc_V\Delta T = nc_P\Delta T - P(V_2 - V_1)$$

From the ideal gas law, $PV_1 = nRT_1$ and $PV_2 = nRT_2$; thus,

$$nc_V\Delta T = nc_P\Delta T - nR\Delta T$$

$$c_V = c_P - R$$

$$c_P = c_V + R$$

For a monatomic ideal gas, this shows that $c_P = \tfrac{5}{2}\,R$. It is important to use the proper units for R in these expressions for c_V and c_P. If heat is to be measured in joules, R must be expressed as

$$R = 8.315 \text{ J K}^{-1} \text{ mol}^{-1}$$

For a diatomic or polyatomic ideal gas, c_V is greater than $\frac{3}{2}R$, because energy can be stored in rotational and vibrational motions of the molecules; a greater amount of heat must be transferred to achieve a given temperature change. Even so, it is still true that

$$c_P = c_V + R \text{ (any ideal gas)} \qquad [12.9]$$

and that internal energy changes depend only on the temperature change; therefore, for a small temperature change ΔT,

$$\Delta U = nc_V\Delta T \text{ (any ideal gas)} \qquad [12.10]$$

For an ideal gas process,

$$\begin{aligned} \Delta H = \Delta U + \Delta(PV) &= nc_V\Delta T + nR\Delta T \\ \Delta H &= nc_P\Delta T \text{ (ideal gas)} \end{aligned} \qquad [12.11]$$

because $c_P = c_V + R$. This result holds for any ideal gas process and shows that enthalpy changes, like internal energy changes, depend only on the temperature difference between initial and final states. These statements are not valid for systems other than ideal gases.

EXAMPLE 12.4

Suppose that 1.00 kJ of heat is transferred to 2.00 mol argon (at 298 K, 1 atm). What will the final temperature T_f be if the heat is transferred (**a**) at constant volume, or (**b**) at constant pressure? Calculate the energy change, ΔU, in each case.

SOLUTION

Because argon is a monatomic, approximately ideal gas,

$$c_V = \tfrac{3}{2}R = 12.47 \text{ J K}^{-1}\text{ mol}^{-1}$$

$$c_P = \tfrac{5}{2}R = 20.79 \text{ J K}^{-1}\text{ mol}^{-1}$$

At constant volume,

$$\begin{aligned} q_V &= nc_V\Delta T \\ 1000 \text{ J} &= (2.00 \text{ mol})(12.47 \text{ J K}^{-1}\text{ mol}^{-1})\Delta T \\ \Delta T &= 40.1 \text{ K}; T_f = 298 + 40.1 = 338 \text{ K} \\ \Delta U &= nc_V\Delta T = q_V = 1000 \text{ J} \end{aligned}$$

At constant pressure,

$$\begin{aligned} q_P &= nc_P\Delta T \\ 1000 \text{ J} &= (2.00 \text{ mol})(20.79 \text{ J K}^{-1}\text{ mol}^{-1})\Delta T \\ \Delta T &= 24.0 \text{ K}; T_f = 298 + 24.0 = 322 \text{ K} \\ \Delta U &= nc_V\Delta T = (2.00 \text{ mol})(12.47 \text{ J K}^{-1}\text{ mol}^{-1})(24 \text{ K}) = 600 \text{ J} \end{aligned}$$

Note that the expression for ΔU involves c_V even though the process is conducted at constant pressure. The difference of 400 J between the input q_P and ΔU is the work done by the gas as it expands.

Related Problems: 17, 18, 19, 20, 21, 22

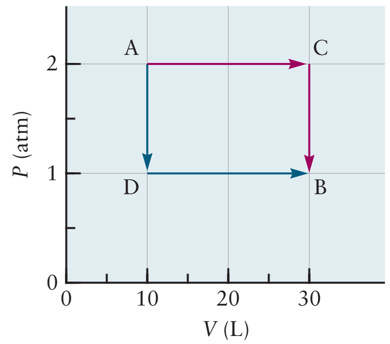

FIGURE 12.10 States A and B of a system are connected by two different ideal-gas processes, one passing through state C and the other through state D.

Heat and Work for Ideal Gases

Now we have all the data needed to calculate heat and work for a variety of processes involving an ideal gas. To illustrate that q and w individually depend on the path followed, but their sum does not, consider the expansion of 1.00 mol of an ideal monatomic gas following two different paths. The system begins at state A ($P_A = 2.00$ atm, $V_A = 10.0$ L) and reaches a final state, B ($P_B = 1.00$ atm, $V_B = 30.0$ L), via either of two paths shown in Figure 12.10. Along path ACB (red arrows in Fig. 12.10), the system is first heated at constant pressure ($P_{ext} = P_A = 2$ atm) until the volume has tripled; then it is cooled at constant volume until the pressure is halved. Along path ADB (blue arrows in Fig. 12.10), the system is cooled at constant volume until the pressure is halved, and then heated at constant pressure ($P_{ext} = P_B = 1$ atm) until the volume has tripled.

The calculations of heat and work for each step are of the type already performed and are straightforward. Thus,

$$w_{AC} = -P_{ext}\Delta V = -P_A(V_B - V_A)$$

$$w_{CB} = 0 \text{ because } V_C = V_B$$

$$q_{AC} = q_P = nc_P\Delta T = \tfrac{5}{2}\, nR(T_C - T_A)$$

$$q_{CB} = q_V = nc_V\Delta T = \tfrac{3}{2}\, nR(T_B - T_C)$$

From the ideal gas law, $nRT_A = P_AV_A$, $nRT_B = P_BV_B$, and $nRT_C = P_CV_C = P_AV_B$ (because $P_A = P_C$ and $V_B = V_C$). Using these relations and summing over the two steps give

$$w_{ACB} = w_{AC} + w_{CB} = -P_A(V_B - V_A) = -40.0 \text{ L atm} = -4050 \text{ J}$$

$$\begin{aligned} q_{ACB} &= q_{AC} + q_{CB} = \tfrac{5}{2}\, nR(T_C - T_A) + \tfrac{3}{2}\, nR(T_B - T_C) \\ &= \tfrac{5}{2}\, P_A(V_B - V_A) + \tfrac{3}{2}\, V_B(P_B - P_A) = (100.0 - 45.0) \text{ L atm} = 5570 \text{ J} \end{aligned}$$

The sum of these is $\Delta U = w_{ACB} + q_{ACB} = 1520$ J. (This could also have been obtained by using the ideal gas law to calculate the initial and final temperatures T_A and T_B.)

The corresponding calculation for path ADB gives

$$w_{ADB} = -2030 \text{ J and } q_{ADB} = 3550 \text{ J}$$

Even though both the work and the heat have changed, their sum is still 1520 J, illustrating that U is a state function, whereas q and w are not.

12.5 Thermochemistry

Up to this point, all the energy changes we have considered are simple physical processes that involve direct mechanical work on a system (as in the paddle wheel driven by a falling weight) or direct thermal contact between two systems at different temperatures. The same methods apply to the heat given off or taken up in the course of a chemical reaction. The study of these heat transfers during chemical reactions is referred to as **thermochemistry.** Because chemical reactions are usually studied at constant pressure, heat transfers in reactions are measured at constant pressure. We obtain these numbers by conducting the chemical reaction in a constant-pressure calorimeter and measuring the heat transferred as q_P. This number is the enthalpy change of the reaction, viewed as a thermodynamic process:

$$q_P = \Delta H = H_f - H_i = H_{products} - H_{reactants} = \Delta H_{reaction}$$

The tabulated values are called **reaction enthalpies.**

Enthalpies of Reaction

When carbon monoxide is burned in oxygen to produce carbon dioxide,

$$\mathrm{CO}(g) + \tfrac{1}{2}\,\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$$

heat is given off. Because this energy is transferred out of the reaction vessel (the system) and into the surroundings, it has a *negative* sign. Careful calorimetric measurements show that 1.000 mol CO reacted completely with 0.500 mol O_2, at 25°C and a constant pressure of 1 atm, leads to an enthalpy change of

$$\Delta H = q_{\mathrm{P}} = -2.830 \times 10^5\ \mathrm{J} = -283.0\ \mathrm{kJ}$$

The kilojoule (kJ), equal to 10^3 J, is used because most enthalpy changes for chemical reactions lie in the range of thousands of joules per mole.

When heat is given off by a reaction (ΔH is negative), the reaction is said to be **exothermic** (Fig. 12.11). Reactions in which heat is taken up (ΔH positive) are called **endothermic** (Fig. 12.12). One example of an endothermic reaction is the preceding reaction written in the opposite direction:

$$\mathrm{CO_2}(g) \longrightarrow \mathrm{CO}(g) + \tfrac{1}{2}\,\mathrm{O_2}(g) \qquad \Delta H = +283.0\ \mathrm{kJ}$$

If the direction of a chemical reaction is reversed, the enthalpy change reverses sign. Heat is required to convert CO_2 to CO and O_2 at constant pressure. The decomposition of CO_2 into CO and O_2 is difficult to perform in the laboratory, whereas the reverse reaction is straightforward. Thermodynamics allows us to predict ΔH of the decomposition reaction with complete confidence, even if a calorimetric experiment is never actually performed for it.

Chemists have agreed on a convention for attaching reaction enthalpy values to balanced chemical equations. A reaction enthalpy written after a balanced chemical equation refers to the enthalpy change for the complete conversion of stoichiometric amounts of reactants to products; the numbers of moles of


(a) (b) (c)

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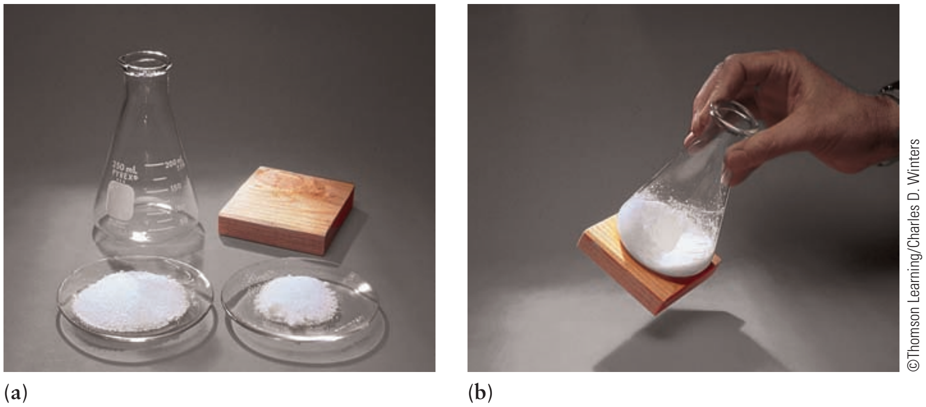
FIGURE 12.11 The thermite reaction, $2\,\mathrm{Al}(s) + \mathrm{Fe_2O_3}(s) \longrightarrow 2\,\mathrm{Fe}(s) + \mathrm{Al_2O_3}(s)$, is among the most exothermic of all reactions, liberating 16 kJ of heat for every gram of aluminum that reacts. (a) A piece of burning magnesium acts as a source of ignition when inserted into a pot containing a finely divided mixture of aluminum powder and iron(III) oxide. (b) After the ignition, the reaction continues on its own. (c) Enough heat is generated to produce molten iron, which can be seen flowing out of the broken pot onto the protective mat and the bottom of the stand.



(a) (b)

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FIGURE 12.12 (a) When mixed in a flask, the two solids $Ba(OH)_2 \cdot 8H_2O(s)$ and $NH_4NO_3(s)$ undergo an acid–base reaction: $Ba(OH)_2 \cdot 8\,H_2O(s) + 2\,NH_4NO_3(s) \longrightarrow Ba(NO_3)_2\,(aq) + 2\,NH_3(aq) + 10\,H_2O(\ell)$. (b) The water produced dissolves excess ammonium nitrate in an endothermic reaction. The dissolution absorbs so much heat that the water on the surface of the wet wooden block freezes to the bottom of the flask, and the block can be lifted up with the flask.

reactants and products are given by the coefficients in the equation. The preceding equation shows the enthalpy change when 1 mol CO_2 is converted to 1 mol CO and $\frac{1}{2}$ mol O_2. If this equation is multiplied by a factor of 2, the enthalpy change must also be doubled because twice as many moles are then involved (enthalpy, like energy, is an *extensive* property).

$$2\,CO_2(g) \longrightarrow 2\,CO(g) + O_2(g) \qquad \Delta H = +566.0\text{ kJ}$$

The molar amounts need not be integers, as the following example illustrates.

EXAMPLE 12.5

Red phosphorus reacts with liquid bromine in an exothermic reaction (Fig. 12.13):

$$2\,P(s) + 3\,Br_2(\ell) \longrightarrow 2\,PBr_3(g) \qquad \Delta H = -243\text{ kJ}$$

Calculate the enthalpy change when 2.63 g phosphorus reacts with an excess of bromine in this way.

SOLUTION

First, convert from grams of phosphorus to moles, using the molar mass of phosphorus, 30.97 g mol^{-1}:

$$\text{moles P} = \frac{2.63\text{ g P}}{30.97\text{ g mol}^{-1}} = 0.0849\text{ mol}$$

Given that an enthalpy change of −243 kJ is associated with 2 mol P, it is readily seen that the enthalpy change associated with 0.0849 mol is

$$\Delta H = 0.0849\text{ mol P} \times \left(\frac{-243\text{ kJ}}{2\text{ mol P}}\right) = -10.3\text{ kJ}$$

Related Problems: 23, 24, 25, 26

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FIGURE 12.13 Red phosphorus reacts exothermically in liquid bromine. The rising gases are a mixture of the product PBr_3 and unreacted bromine that has boiled off.

The enthalpy change for the reaction of 1 mol carbon monoxide with oxygen was stated to be −283.0 kJ. In a second experiment, the heat evolved when 1 mol carbon (graphite) is burned in oxygen to carbon dioxide at 25°C is readily measured to be

$$C(s,gr) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5\text{ kJ}$$

Now, suppose we need to know the enthalpy change for the reaction

$$C(s,gr) + \tfrac{1}{2}\,O_2(g) \longrightarrow CO(g) \qquad \Delta H = ?$$

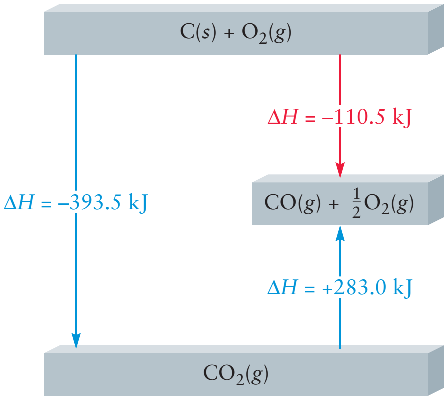

FIGURE 12.14 Because enthalpy is a state property, the enthalpy change for the reaction of carbon with oxygen to give carbon monoxide (red arrow) can be determined through measurements along a path that is less direct but easier to study (blue arrows). The enthalpy change sought is the sum of the enthalpy change to burn carbon to carbon dioxide and that to convert carbon dioxide to carbon monoxide and oxygen.

This reaction cannot be performed simply in the laboratory. If 1 mol graphite is heated with $\frac{1}{2}$ mol oxygen, almost half the carbon burns to $CO_2(g)$ and the remainder is left as unreacted carbon. Nevertheless, thermodynamics allows us to predict the heat that *would* evolve if we could perform the reaction as written. This is possible because H is a state function, and thus ΔH for the reaction is independent of the path followed from reactants to products. We are free to select any path for which we have all the data needed for the calculation. In Figure 12.14, we illustrate the path in which 1 mol C is burned with O_2 to CO_2 (with $\Delta H = -393.5$ kJ), and to this is added the calculated enthalpy change for the (hypothetical) process in which CO_2 is converted to CO and O_2 ($\Delta H = +283.0$ kJ). The total ΔH is the algebraic sum of the two known enthalpy changes, $-393.5 \text{ kJ} + 283.0 \text{ kJ} = -110.5$ kJ. To see this more clearly, the reactions are written out as follows:

$$\begin{array}{lr} \mathrm{C}(s, \mathrm{gr}) + \mathrm{O}_2(g) \longrightarrow \mathrm{CO}_2(g) & \Delta H_1 = -393.5 \text{ kJ} \\ \mathrm{CO}_2(g) \longrightarrow \mathrm{CO}(g) + \frac{1}{2}\mathrm{O}_2(g) & \Delta H_2 = +283.0 \text{ kJ} \\ \hline \mathrm{C}(s, \mathrm{gr}) + \frac{1}{2}\mathrm{O}_2(g) \longrightarrow \mathrm{CO}(g) & \Delta H = \Delta H_1 + \Delta H_2 = -110.5 \text{ kJ} \end{array}$$

If two or more chemical equations are added to give another chemical equation, the corresponding enthalpies of reaction must be added.

This statement is known as **Hess's law** and derives from the fact that enthalpy is a state function. It is proper to include in the pathway any convenient reaction for which the enthalpy change is known, even if that reaction is difficult to study directly and its enthalpy change is known only from studies of the reverse reaction. The step labeled (hypothetical) above is a good example.

The corresponding internal energy change ΔU might be desired for this reaction. The quantity ΔU is simple to calculate because of the relation

$$\Delta H = \Delta U + \Delta(PV)$$

or

$$\Delta U = \Delta H - \Delta(PV)$$

The gases can be assumed to obey the ideal gas law, so

$$\Delta(PV) = \Delta(nRT) = RT\,\Delta n_{\mathrm{g}}$$

because the temperature is constant at 25°C. Here, Δn_{g} is the change in the number of moles of *gas* in the reaction as written:

$$\begin{aligned} \Delta n_{\mathrm{g}} &= \text{total moles of product gases} - \text{total moles of reactant gases} \\ &= 1 \text{ mol} - \tfrac{1}{2} \text{ mol} = \tfrac{1}{2} \text{ mol} \end{aligned}$$

(Graphite is a solid, and its volume is negligible compared with the volumes of the gases.) Hence,

$$\Delta(PV) = RT\,\Delta n_{\mathrm{g}} = (8.315 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})(\tfrac{1}{2} \text{ mol}) = 1.24 \times 10^3 \text{ J} = 1.24 \text{ kJ}$$

Note that R must be expressed in J K^{-1} mol^{-1} to obtain the result in joules. Therefore,

$$\Delta U = -110.5 \text{ kJ} - 1.24 \text{ kJ} = -111.7 \text{ kJ}$$

For reactions in which only liquids and solids are involved, or those in which the number of moles of gas does not change, the enthalpy and energy changes are almost equal and their difference can be neglected.

Phase changes are not chemical reactions, but their enthalpy changes can be analyzed in the same way. Heat must be absorbed by ice to transform to water, so the phase change is endothermic, with ΔH positive:

$$\mathrm{H_2O}(s) \longrightarrow \mathrm{H_2O}(\ell) \qquad \Delta H_{\mathrm{fus}} = +6.007 \text{ kJ mol}^{-1}$$

TABLE 12.2 Enthalpy Changes of Fusion and Vaporization†

Substance	ΔH_{fus} (kJ mol^{-1})	ΔH_{vap} (kJ mol^{-1})
NH_3	5.650	23.35
HCl	1.992	16.15
CO	0.836	6.04
CCl_4	2.500	30.00
H_2O	6.007	40.66
NaCl	28.800	170.00

†The enthalpy changes are measured at the normal melting point and the normal boiling point, respectively.

Here, ΔH_{fus} is the **molar enthalpy of fusion,** the heat that must be transferred at constant pressure to melt 1 mole of substance. When a liquid freezes, the reaction is reversed and an equal amount of heat is given off to the surroundings; that is, $\Delta H_{freez} = -\Delta H_{fus}$. The vaporization of 1 mole of liquid at constant pressure and temperature requires an amount of heat called the **molar enthalpy of vaporization,** ΔH_{vap},

$$H_2O(\ell) \longrightarrow H_2O(g) \qquad \Delta H_{vap} = +40.7 \text{ kJ mol}^{-1}$$

whereas the condensation of a liquid from a vapor is an exothermic process, with $\Delta H_{cond} = -\Delta H_{vap}$. Table 12.2 lists enthalpies of fusion and vaporization.

EXAMPLE 12.6

To vaporize 100.0 g carbon tetrachloride at its normal boiling point, 349.9 K, and $P = 1$ atm, 19.5 kJ of heat is required. Calculate ΔH_{vap} for CCl_4 and compare it with ΔU for the same process.

SOLUTION

The molar mass of CCl_4 is 153.8 g mol^{-1}; thus, the number of moles in 100.0 g is

$$\frac{100.0 \text{ g } CCl_4}{153.8 \text{ g mol}^{-1}} = 0.6502 \text{ mol } CCl_4$$

The enthalpy change for 1 mol CCl_4 is then

$$\left(\frac{19.5 \text{ kJ}}{0.6502 \text{ mol } CCl_4}\right) \times 1.00 \text{ mol } CCl_4 = 30.0 \text{ kJ} = \Delta H_{vap}$$

The energy change is then

$$\Delta U = \Delta H_{vap} - \Delta(PV) = \Delta H_{vap} - RT\,\Delta n_g$$

Inserting $T = 349.9$ K and $\Delta n_g = 1$ (because there is an increase of 1 mol of gaseous products for each mole of liquid that is vaporized) gives

$$\begin{aligned}\Delta U &= 30.0 \text{ kJ} - (8.315 \text{ J K}^{-1} \text{ mol}^{-1})(349.9 \text{ K})(1.00 \text{ mol})(10^{-3} \text{ kJ J}^{-1}) \\ &= (30.0 - 2.9) \text{ kJ} = +27.1 \text{ kJ mol}^{-1}\end{aligned}$$

Thus, of the 30.0 kJ of energy transferred from the surroundings in the form of heat, 27.1 kJ is used to increase the internal energy of the molecules (ΔU) and 2.9 kJ is used to expand the resulting vapor, $\Delta(PV)$.

Related Problems: 27, 28, 29, 30

Standard-State Enthalpies

Absolute values of the enthalpy of a substance, like absolute values of the internal energy, cannot be measured or calculated. Only *changes* in enthalpy can be measured. Just as altitudes are measured relative to a standard altitude (sea level), it is necessary to adopt a reference state for the enthalpies of substances. To cope with this problem, chemists define **standard states** for chemical substances as follows:

> For solids and liquids, the standard state is the thermodynamically stable state at a pressure of 1 atm and at a specified temperature.
>
> For gases, the standard state is the gaseous phase at a pressure of 1 atm, at a specified temperature and exhibiting ideal gas behavior.
>
> For dissolved species, the standard state is a 1-M solution at a pressure of 1 atm, at a specified temperature and exhibiting ideal solution behavior.

Standard-state values of enthalpy and other quantities are designated by attaching a superscript ° (pronounced "naught") to the symbol for the quantity and writing the specified temperature as a subscript. Any temperature may be chosen as the "specified temperature." The most common choice is 298.15 K (25°C exactly); if the temperature of a standard state is not explicitly indicated, 298.15 K should be assumed to be the value.

Once standard states have been defined, the zero of the enthalpy scale is defined by arbitrarily setting the enthalpies of selected reference substances to zero in their standard states. This is completely analogous to assigning zero as the altitude at sea level. Chemists have agreed to the following: *The chemical elements in their standard states at 298.15 K have zero enthalpy.* A complication immediately arises because some elements exist in various allotropic forms that differ in structure and all physical properties, including enthalpy. For example, oxygen can be prepared as $O_2(g)$ or $O_3(g)$ (ozone), and carbon exists in numerous allotropic forms, including graphite, diamond, and the fullerenes (see Section 7.8). Chemists have agreed to assign zero enthalpy to the form that is most stable at 1 atm and 298.15 K. Thus, $O_2(g)$ is assigned zero enthalpy in its standard state at 298.15 K, whereas $O_3(g)$ has nonzero enthalpy in its standard state at 298.15 K. The most stable form of carbon at 1 atm and 298.15 K is graphite, which is assigned zero enthalpy; diamond and all the fullerenes are assigned nonzero enthalpy.[2]

The enthalpy change for a chemical reaction in which all reactants and products are in their standard states and at a specified temperature is called the **standard enthalpy** (written $\Delta H°$) for that reaction. The standard enthalpy is the central tool in thermochemistry because it provides a systematic means for comparing the energy changes due to bond rearrangements in different reactions. Standard enthalpies can be calculated from tables of reference data. For this purpose, we need one additional concept. The **standard enthalpy of formation** ΔH_f° of a compound is defined to be the enthalpy change for the reaction that produces 1 mol of the compound from its elements in their stable states, all at 25°C and 1 atm pressure. For example, the standard enthalpy of formation of liquid water is the enthalpy change for the reaction

$$H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow H_2O(\ell) \qquad \Delta H^\circ = -285.83 \text{ kJ}$$

$$\Delta H_f^\circ(H_2O(\ell)) = -285.83 \text{ kJ mol}^{-1}$$

Here, the superscript ° indicates standard-state conditions, and the subscript f stands for *formation.*

The ΔH_f° for an *element* that is already in its standard state is clearly zero, because no further change is needed to bring it to standard-state conditions. But the

---

[2] There is one exception to this choice of standard state. The standard state of phosphorus is taken to be white phosphorus, rather than the more stable red or black form, because the latter are less well characterized and less reproducible in their properties.

standard enthalpy of formation of a mole of *atoms* of an element is often a large positive quantity. That is, the reaction to generate them is endothermic:

$$\tfrac{1}{2}\,\mathrm{H_2}(g) \longrightarrow \mathrm{H}(g) \qquad \Delta H^\circ = +217.96 \text{ kJ}$$

$$\Delta H_\mathrm{f}^\circ(\mathrm{H}(g)) = 217.96 \text{ kJ mol}^{-1}$$

For dissolved species the standard state is defined as an ideal solution with a concentration of 1 M (this is obtained in practice by extrapolating the dilute solution behavior up to this concentration). A special comment is in order on the standard enthalpies of formation of ions. When a strong electrolyte dissolves in water, both positive and negative ions form; it is impossible to produce one without the other. It is therefore also impossible to measure the enthalpy change of formation of ions of only one charge. Only the sum of the enthalpies of formation of the positive and negative ions is accessible to calorimetric experiments. Therefore, chemists have agreed that $\Delta H_\mathrm{f}^\circ$ of $\mathrm{H}^+(aq)$ is set to zero.

Tables of $\Delta H_\mathrm{f}^\circ$ for compounds are the most important data source for thermochemistry. From them it is easy to calculate ΔH° for reactions of the compounds, and thereby systematically compare the energy changes due to bond rearrangements in different reactions. Appendix D gives a short table of standard enthalpies of formation at 25°C. The following example shows how they can be used to determine enthalpy changes for reactions performed at 25°C and 1 atm pressure.

EXAMPLE 12.7

Using Appendix D, calculate ΔH° for the following reaction at 25°C and 1 atm pressure:

$$2\ \mathrm{NO}(g) + \mathrm{O_2}(g) \longrightarrow 2\ \mathrm{NO_2}(g)$$

SOLUTION

Because enthalpy is a function of state, ΔH can be calculated along any convenient path. In particular, two steps can be chosen for which ΔH is found easily. In step 1, the reactants are decomposed into the elements in their standard states:

$$2\ \mathrm{NO}(g) \longrightarrow \mathrm{N_2}(g) + \mathrm{O_2}(g) \qquad \Delta H_1 = -2\ \Delta H_\mathrm{f}^\circ(\mathrm{NO})$$

The minus sign appears because the process chosen is the reverse of the formation of NO; the factor of 2 is present because 2 mol NO is involved. Because oxygen is already an element in its standard state, it does not need to be changed [equivalently, $\Delta H_\mathrm{f}^\circ(\mathrm{O_2}(g))$ is 0].

In step 2, the elements are combined to form products:

$$\mathrm{N_2}(g) + 2\ \mathrm{O_2}(g) \longrightarrow 2\ \mathrm{NO_2}(g) \qquad \Delta H_1 = 2\ \Delta H_\mathrm{f}^\circ(\mathrm{NO_2})$$

The enthalpy change of the overall reaction is then the sum of these two enthalpies:

$$\begin{aligned}\Delta H^\circ &= \Delta H_1 + \Delta H_2 = -2\ \Delta H_\mathrm{f}^\circ(\mathrm{NO}) + 2\ \Delta H_\mathrm{f}^\circ(\mathrm{NO_2}) \\ &= -(2 \text{ mol})(90.25 \text{ kJ mol}^{-1}) + (2 \text{ mol})(33.18 \text{ kJ mol}^{-1}) = -114.14 \text{ kJ}\end{aligned}$$

Related Problems: 35, 36, 37, 38

The general pattern should be clear from this example. The change ΔH° for a reaction at atmospheric pressure and 25°C is the sum of the $\Delta H_\mathrm{f}^\circ$ for the *products* (multiplied by their coefficients in the balanced chemical equation) minus the sum of the $\Delta H_\mathrm{f}^\circ$ for the *reactants* (also multiplied by their coefficients). For a general reaction of the form

$$a\mathrm{A} + b\mathrm{B} \longrightarrow c\mathrm{C} + d\mathrm{D}$$

the standard enthalpy change is

$$\Delta H^\circ = c\,\Delta H_f^\circ(\mathrm{C}) + d\,\Delta H_f^\circ(\mathrm{D}) - a\,\Delta H_f^\circ(\mathrm{A}) - b\,\Delta H_f^\circ(\mathrm{B})$$

This equation can be extended to calculate the standard-state enthalpy change for any chemical reaction by adding up the standard-state enthalpy of formation for all the products (each multiplied by its stoichiometric coefficient in the balanced chemical equation) and subtracting off the total for all the reactants (each multiplied by its stoichiometric coefficient in the balanced chemical equation). In mathematical form, this procedure is represented by the equation

$$\Delta H^\circ = \sum_{i=1}^{prod} n_i \Delta H_i^\circ - \sum_{j=1}^{react} n_j \Delta H_j^\circ \qquad [12.12]$$

Bond Enthalpies

Chemical reactions between molecules require existing bonds to break and new ones to form in a new arrangement of the atoms. Chemists have developed methods to study highly reactive intermediates, species in which bonds have been broken and not yet re-formed. For example, a hydrogen atom can be removed from a methane molecule,

$$CH_4(g) \longrightarrow CH_3(g) + H(g)$$

leaving two fragments, neither of which has a stable valence electron structure in the Lewis electron dot picture. Both will go on to react rapidly with other molecules or fragments and eventually form the stable products of that reaction. Nonetheless, we can measure many of the properties of these reactive species during the short time they are present.

One such important measurable quantity is the enthalpy change when a bond is broken in the gas phase, called the **bond enthalpy.** This is invariably positive because heat must be added to a collection of stable molecules to break their bonds. For example, the bond enthalpy of a C—H bond in methane is 438 kJ mol^{-1}, measured as the standard enthalpy change for the reaction

$$CH_4(g) \longrightarrow CH_3(g) + H(g) \qquad \Delta H^\circ = +438\ \mathrm{kJ}$$

in which 1 mol of C—H bonds is broken, one for each molecule of methane. Bond enthalpies are fairly reproducible from one compound to another. Each of the following gas-phase reactions involves the breaking of a C—H bond:

$$C_2H_6(g) \longrightarrow C_2H_5(g) + H(g) \qquad \Delta H^\circ = +410\ \mathrm{kJ}$$

$$CHF_3(g) \longrightarrow CF_3(g) + H(g) \qquad \Delta H^\circ = +429\ \mathrm{kJ}$$

$$CHCl_3(g) \longrightarrow CCl_3(g) + H(g) \qquad \Delta H^\circ = +380\ \mathrm{kJ}$$

$$CHBr_3(g) \longrightarrow CBr_3(g) + H(g) \qquad \Delta H^\circ = +377\ \mathrm{kJ}$$

The approximate constancy of the measured enthalpy changes (all lie within 8% of their average value) suggests that the C—H bonds in all five molecules are similar. Because such bond enthalpies are reproducible from one molecule to another, it is useful to tabulate *average* bond enthalpies from measurements on a series of compounds (Table 12.3). Any given bond enthalpy will differ somewhat from those shown, but in most cases, the deviations are small. The reproducibility of bond energies in a series of molecules was introduced in Section 3.5, and representative values were listed in Table 3.4. Bond energy values are related to bond enthalpy values by the relation $\Delta H = \Delta U + \Delta(PV)$, described in the paragraphs following Example 12.5.

TABLE 12.3 Average Bond Enthalpies

	Molar Enthalpy of Atomization (kJ mol^{-1})‡	Bond Enthalpy (kJ mol^{-1})†								
		H—	C—	C═	C≡	N—	N═	N≡	O—	O═
H	218.0	436	413			391			463	
C	716.7	413	348	615	812	292	615	891	351	728
N	472.7	391	292	615	891	161	418	945		
O	249.2	463	351	728					139	498
S	278.8	339	259	477						
F	79.0	563	441			270			185	
Cl	121.7	432	328			200			203	
Br	111.9	366	276							
I	106.8	299	240							

†From Appendix D.
‡Data from L. Pauling. *The Nature of the Chemical Bond,* 3rd ed. Ithaca, NY: Cornell University Press, 1960.

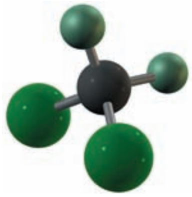

FIGURE 12.15 Dichlorodifluoromethane, CCl_2F_2, also known as Freon-12.

The bond enthalpies in Table 12.3 can be used, together with enthalpies of atomization of the elements from the same table, to estimate standard enthalpies of formation ΔH_f° for molecules in the gas phase and enthalpy changes ΔH° for gas-phase reactions. This is illustrated by the following example.

EXAMPLE 12.8

Estimate the standard enthalpy of formation of dichlorodifluoromethane, $CCl_2F_2(g)$ (Fig. 12.15). This compound is also known as Freon-12 and has been used as a refrigerant because of its low reactivity and high volatility. It and other related chlorofluorocarbons (CFCs) are being phased out because of their role in depleting the ozone layer in the outer atmosphere, as discussed in Section 20.5.

SOLUTION

The standard enthalpy of formation of $CCl_2F_2(g)$ is the enthalpy change for the process in which it is formed from the elements in their standard states at 25°C:

$$C(s,\text{gr}) + Cl_2(g) + F_2(g) \longrightarrow CCl_2F_2(g)$$

This reaction can be replaced by a hypothetical two-step process: All the species appearing on the left are atomized, and then the atoms are combined to make CCl_2F_2.

$$C(s,\text{gr}) + Cl_2(g) + F_2(g) \longrightarrow C(g) + 2\ Cl(g) + 2\ F(g)$$

$$C(g) + 2\ Cl(g) + 2\ F(g) \longrightarrow CCl_2F_2(g)$$

The enthalpy change ΔH_1 for the first step is the sum of the atomization energies:

$$\Delta H_1 = \Delta H_f^\circ(C(g)) + 2\ \Delta H_f^\circ(Cl(g)) + 2\ \Delta H_f^\circ(F(g))$$

$$= 716.7 + 2(121.7) + 2(79.0) = 1118 \text{ kJ}$$

The enthalpy change ΔH_2 for the second step can be estimated from the bond enthalpies of Table 12.3. This step involves the formation (with release of heat and, therefore, negative enthalpy change) of two C—Cl and two C—F bonds per molecule. The net ΔH for this step is then

$$\Delta H_2 \approx -[2(328) + 2(441)] = -1538 \text{ kJ}$$

$$\Delta H_1 + \Delta H_2 = -1538 + 1118 = -420 \text{ kJ}$$

This ΔH_f°, −420 kJ mol^{-1}, compares fairly well with the experimental value, −477 kJ mol^{-1}. In general, much better agreement than this is not to be expected, because tabulated bond enthalpies are only average values.

Related Problems: 45, 46, 47, 48

12.6 Reversible Processes in Ideal Gases

Most thermodynamic processes conducted in laboratory work are irreversible, in the sense of Section 12.1. Except in the initial and final states, the system is not at equilibrium, and the equation of state relationship between observable properties does not exist. Consequently, changes in thermodynamic quantities during an irreversible process cannot in general be calculated. Nonetheless, the changes in those quantities that are state functions are well defined, as long as the initial and final equilibrium states are known. Because these changes are independent of the detailed path of the process, they can be evaluated for any known process that connects these initial and final states. Changes can be directly calculated along *reversible* paths, during which the system proceeds through a sequence of equilibrium states in which observable properties are related by the equation of state.

This section demonstrates calculations of changes in macroscopic properties caused during several specific reversible processes in ideal gases. These will serve as auxiliary calculation pathways for evaluating changes in state functions during irreversible processes. We use this procedure extensively in Chapter 13 on spontaneous processes and the second law of thermodynamics.

Recall from Section 12.1 that a true reversible process is an idealization; it is a process in which the system proceeds with infinitesimal speed through a series of equilibrium states. The external pressure P_{ext}, therefore, can never differ by more than an infinitesimal amount from the pressure, P, of the gas itself. The heat, work, energy, and enthalpy changes for ideal gases at constant volume (called **isochoric processes**) and at constant pressure **(isobaric processes)** have already been considered. This section examines *isothermal* (constant temperature) and *adiabatic* ($q = 0$) processes.

Isothermal Processes

An **isothermal process** is one conducted at constant temperature. This is accomplished by placing the system in a large reservoir (bath) at fixed temperature and allowing heat to be transferred as required between system and reservoir. The reservoir is large enough that its temperature is almost unchanged by this heat transfer. In Section 12.4, U for an ideal gas was shown to depend only on temperature; therefore, $\Delta U = 0$ for any isothermal ideal gas process. From the first law it follows that

$$w = -q \text{ (isothermal process, ideal gas)}$$

In a *reversible* process, $P_{\text{ext}} = P_{\text{gas}} \equiv P$. But the relation $w = -P_{\text{ext}}\,\Delta V$ from Section 12.2 cannot be used to calculate the work, because that expression applies only if the external pressure remains constant as the volume changes. In the reversible isothermal expansion of an ideal gas,

$$P_{\text{ext}} = P = \frac{nRT}{V} \qquad [12.13]$$

By Boyle's law, the pressure falls as the volume is increased from V_1 to V_2, as shown by the solid line in Figure 12.16. In this case, the work is calculated by approximating the process as a *series* of expansions by small amounts ΔV, during each of which P_{ext} is held constant at P_i, with $i = 1, 2, 3,$ and so on labeling the step. The work done in step i is $-P_i\delta V$, and thus the total work done is the sum of the work in all steps:

$$w = -P_1\delta V - P_2\delta V - \cdots$$

The work in the complete process is the sum of the areas of the rectangles in the figure. As the step size δV is made smaller, it approaches the infinitesimal

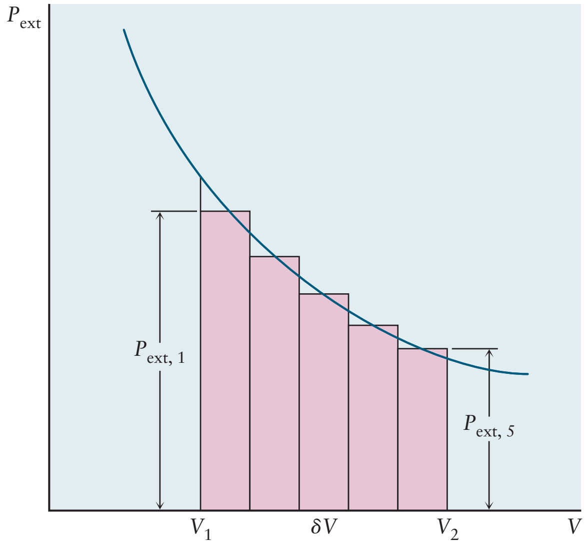

FIGURE 12.16 The area under the graph of external pressure against volume can be approximated as the sum of the areas of the rectangles shown.

volume change that is written dV, and the corresponding increment of work becomes

$$dw = -P_{\text{ext}}\,dV$$

In this limit the sum of the areas of the rectangles approaches the area under the graph of P versus V. This limiting sum is the *integral* of P_{ext} from V_1 to V_2 and is written symbolically using an integral sign:

$$w = -\int_{V_1}^{V_2} P\,dV \quad \text{(reversible process)} \tag{12.14}$$

Note that we used Equation 12.13 to replace P_{ext} with the internal pressure P in this reversible process. This is a compact way of saying that the work, w, for a reversible expansion process is (with a minus sign) the area under the graph of P plotted against V from V_1 to V_2.

Mathematical methods of defining and calculating integrals are beyond the scope of this book, but Appendix C gives some supplementary information about several integrals that are important in chemistry, and it should be read by students unfamiliar with calculus. The main idea is the relation between a thermodynamic quantity (in this case, the work) and the area under a curve.

In this case, the ideal gas law is used to write this area as

$$w = -nRT\int_{V_1}^{V_2} \frac{1}{V}\,dV \tag{12.15}$$

This integral is the area under a graph of $1/V$ against V (a hyperbola) from V_1 to V_2. It defines the *natural logarithm* function, symbolized “ln” (see Appendix C). In particular,

$$\begin{aligned} w &= -nRT\ln\frac{V_2}{V_1} \\ q &= -w = nRT\ln\frac{V_2}{V_1} \\ \Delta U &= 0 \text{ because } \Delta T = 0 \\ \Delta H &= \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) = 0 \end{aligned} \tag{12.16}$$

The enthalpy change, like the energy change, depends only on temperature for an ideal gas.

That V_2 is greater than V_1 implies that $w < 0$ and $q > 0$; in an isothermal expansion, the system does work against the surroundings and heat must be transferred into it to maintain T constant. In an isothermal compression, the reverse is true: The surroundings do work on the system, and the system must then lose heat to the bath to maintain T constant.

EXAMPLE 12.9

Calculate the heat and the work associated with a process in which 5.00 mol of gas expands reversibly at constant temperature $T = 298$ K from a pressure of 10.00 to 1.00 atm.

SOLUTION

At constant T and n, q and w are given by the equations just above Equation 12.16. Inserting the data for this example gives

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} = \frac{10.0 \text{ atm}}{1.00 \text{ atm}} = 10.0$$

Thus,

$$\begin{aligned} w &= -(5.00 \text{ mol})(8.315 \text{ J K}^{-1}\text{ mol}^{-1})(298 \text{ K}) \ln 10.0 \\ &= -2.85 \times 10^4 \text{ J} = -28.5 \text{ kJ} \\ q &= -w = 28.5 \text{ kJ} \end{aligned}$$

Related Problems: 51, 52

Adiabatic Processes

An **adiabatic process** is one in which there is no transfer of heat into or out of the system. This is accomplished by placing an adiabatic wall (thermal insulation) around the system to prevent heat flow.

$$q = 0$$

$$\Delta U = w$$

Consider a small adiabatic change. The volume changes by an amount dV and the temperature by an amount dT. Now U depends only on temperature for an ideal gas, so

$$dU = nc_V\, dT$$

As always, the work is given by $-P_{ext}\, dV$. Setting these equal gives

$$nc_V\, dT = -P_{ext}\, dV$$

In other words, the temperature change dT is related to the volume change dV in such a process.

If the process is *reversible,* as well as adiabatic, so that $P_{ext} \approx P$, the ideal gas law can be used to write

$$nc_V\, dT = -P\, dV = -\frac{nRT}{V}\, dV$$

The equation is simplified by dividing both sides through by nT, making the left side depend only on T and the right side only on V:

$$\frac{c_V}{T}\, dT = -\frac{R}{V}\, dV$$

Suppose now that the change is not infinitesimal but large. How are temperature and volume related in this case? If a series of such infinitesimal changes is added together, the result is an integral of both sides of the equation from the initial state (specified by T_1 and V_1) to the final state (specified by T_2 and V_2):

$$c_V \int_{T_1}^{T_2} \frac{1}{T}\, dT = -R \int_{V_1}^{V_2} \frac{1}{V}\, dV$$

Here, c_V has been assumed to be approximately independent of T over the range from T_1 to T_2. Evaluating the integrals gives

$$c_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} = R \ln \frac{V_1}{V_2}$$

A more useful form results from taking antilogarithms of both sides:

$$\left(\frac{T_2}{T_1}\right)^{c_V} = \left(\frac{V_1}{V_2}\right)^{R} = \left(\frac{V_1}{V_2}\right)^{c_P - c_V}$$

The last step used the fact that $R = c_P - c_V$. Thus,

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{c_P/c_V - 1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

where $\gamma = c_P/c_V$ is the ratio of specific heats. This can be rearranged to give

$$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1} \qquad [12.17]$$

In many situations, the initial thermodynamic state and, therefore, T_1 and V_1 are known. If the final volume V_2 is known, T_2 can be calculated; if T_2 is known, V_2 can be calculated.

In some cases, only the final pressure, P_2, of an adiabatic process is known. In this case, the ideal gas law gives

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

Multiplying this by Equation 12.17 gives

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \qquad [12.18]$$

This can be used to calculate V_2 from a known P_2.

Once the pressure, temperature, and volume of the final state are known, the energy and enthalpy changes and the work done are straightforward to calculate:

$$\Delta U = nc_V(T_2 - T_1) = w \text{ (reversible adiabatic process for ideal gas)}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_2 V_2 - P_1 V_1)$$

or more simply,

$$\Delta H = nc_P \Delta T$$

EXAMPLE 12.10

Suppose 5.00 mol of an ideal monatomic gas at an initial temperature of 298 K and pressure of 10.0 atm is expanded adiabatically and reversibly until the pressure has decreased to 1.00 atm. Calculate the final volume and temperature, the energy and enthalpy changes, and the work done.

SOLUTION

The initial volume is

$$V_1 = \frac{nRT_1}{P_1} = \frac{(5.00\ \text{mol})(0.08206\ \text{L atm K}^{-1}\ \text{mol}^{-1})(298\ \text{K})}{(10.0\ \text{atm})} = 12.2\ \text{L}$$

and the heat capacity ratio for a monatomic gas is

$$\gamma = \frac{c_P}{c_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$$

For a reversible adiabatic process,

$$\frac{P_1}{P_2} V_1^\gamma = V_2^\gamma$$

$$(10.0)(12.2\ \text{L})^{5/3} = V_2^{5/3}$$

$$V_2 = (12.2\ \text{L})(10.0)^{3/5} = 48.7\ \text{L}$$

The final temperature can now be calculated from the ideal gas law:

$$T_2 = \frac{P_2V_2}{nR} = 119\ \text{K}$$

From this the work done and the energy change can be found,

$$w = \Delta U = nc_V\Delta T = (5.00\ \text{mol})(\tfrac{3}{2} \times 8.315\ \text{J K}^{-1}\ \text{mol}^{-1})(119\ \text{K} - 298\ \text{K})$$
$$= -11{,}200\ \text{J}$$

as well as the enthalpy change:

$$\Delta H = nc_P\Delta T = (5.00\ \text{mol})(\tfrac{5}{2} \times 8.315\ \text{J K}^{-1}\ \text{mol}^{-1})(119\ \text{K} - 298\ \text{K}) = -18{,}600\ \text{J}$$

Related Problems: 53, 54

Figure 12.17 compares the adiabatic expansion of this example to the isothermal expansion of Example 12.9. Note that the initial states were the same in the two

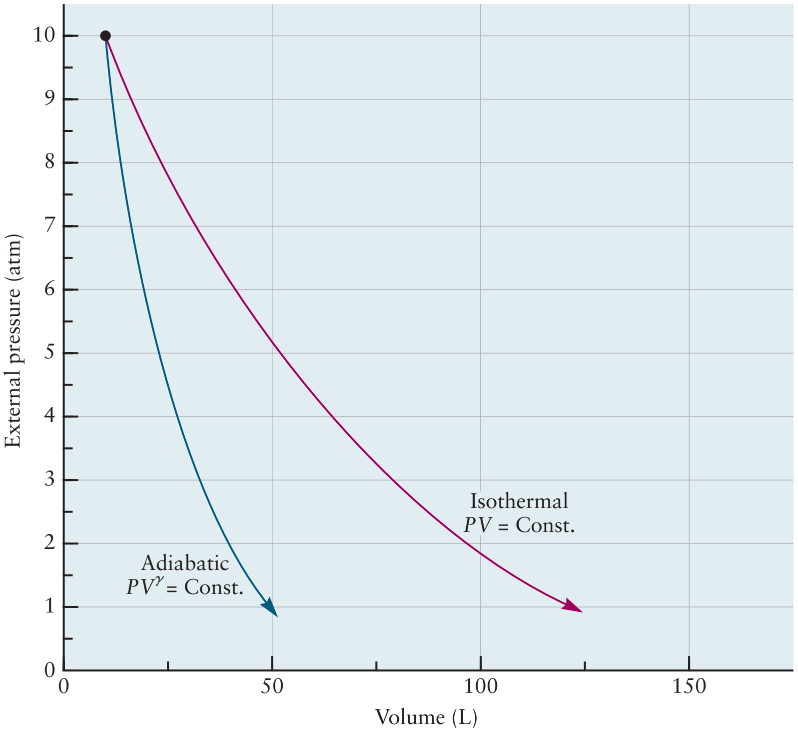

FIGURE 12.17 A comparison of reversible isothermal and adiabatic expansions. Using the technique shown in Figure 12.16, the adiabatic work is 40% of the isothermal work.

cases, as were the final pressures. However, the final volume is larger by more than a factor of 2 for the isothermal expansion, and the work output for the adiabatic case is only 40% of the output from the isothermal expansion. Because $\gamma > 1$, the adiabatic line falls off more rapidly with increasing volume than the isothermal line. Because no heat is transferred in an adiabatic expansion, the work comes from the internal energy of the gas; thus, the temperature declines.

CHAPTER SUMMARY

The central goal of this chapter is to define and measure the heat liberated or absorbed during a chemical reaction. We achieved that goal in Section 12.5 by introducing the enthalpy change of a reaction, which is measured by performing the reaction in a constant-pressure calorimeter. Tabulating data for reactions in which both products and reactants are in their standard states gives the standard enthalpy of reaction, which enables systematic comparison of the energy changes due to bond rearrangements in different reactions. The standard enthalpy change for a reaction is readily calculated from tables of the standard enthalpy of formation for the products and reactants. These basic tools of thermochemistry completely describe the energy transfers in chemical reactions.

The discussion of basic thermodynamics in Sections 12.1 through 12.4 can be viewed as background necessary for achieving the central goal. Even so, this material is important in its own right and will be used repeatedly throughout the book. Similarly, the discussion of reversible isothermal and adiabatic processes in Section 12.6 provides background needed later in the book to calculate changes in state functions for irreversible processes.

CUMULATIVE EXERCISE

Methanol as a Gasoline Substitute

Methanol (CH_3OH) is used as a substitute for gasoline in certain high-performance vehicles. To design engines that will run on methanol, we must understand its thermochemistry.

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A methanol-powered bus.

(a) The methanol in an automobile engine must be in the gas phase before it can react. Calculate the heat (in kilojoules) that must be added to 1.00 kg liquid methanol to increase its temperature from 25.0°C to its normal boiling point, 65.0°C. The molar heat capacity of liquid methanol is 81.6 J K^{-1} mol^{-1}.

(b) Once the methanol has reached its boiling point, it must be vaporized. The molar enthalpy of vaporization for methanol is 38 kJ mol^{-1}. How much heat must be added to vaporize 1.00 kg methanol?

(c) Once it is in the vapor phase, the methanol can react with oxygen in the air according to

$$CH_3OH(g) + \tfrac{3}{2}\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$$

Use average bond enthalpies to estimate the enthalpy change in this reaction, for 1 mol of methanol reacting.

(d) Use data from Appendix D to calculate the actual enthalpy change in this reaction, assuming it to be the same at 65°C as at 25°C.

(e) Calculate the heat released when 1.00 kg gaseous methanol is burned in air at constant pressure. Use the more accurate result of part (d), rather than that of part (c).

Methanol, CH_3OH.

(f) Calculate the *difference* between the change in enthalpy and the change in internal energy when 1.00 kg gaseous methanol is oxidized to gaseous CO_2 and H_2O at 65°C.

(g) Suppose now that the methanol is burned inside the cylinder of an automobile. Taking the radius of the cylinder to be 4.0 cm and the distance moved by the piston during one stroke to be 12 cm, calculate the work done on the gas per stroke as it expands against an external pressure of 1.00 atm. Express your answer in liter-atmospheres and in joules.

Answers

(a) 102 kJ

(b) 1.2×10^3 kJ

(c) -508 kJ

(d) -676.49 kJ

(e) 2.11×10^4 kJ

(f) $\Delta H - \Delta U = 43.9$ kJ

(g) -0.60 L atm $= -61$ J

CHAPTER REVIEW

Systems, States, and Processes

- The system is that part of the universe of interest, for example a chemical reaction, an engine, a human being.
- The surroundings are that part of the universe that exchange matter and energy with the system during a process.
- The thermodynamic universe is the combination of the system and the surroundings for a particular process of interest; it is assumed to be closed and isolated.
- A closed system is one in which no exchange of matter between system and surroundings is permitted.
- An adiabatic system is one in which no exchange of heat between system and surroundings is permitted.
- A thermodynamic state is a condition in which all macroscopic properties of a system are determined by the external conditions imposed on the system (for example, n, T, and P).
- A thermodynamic system is in thermodynamic equilibrium if none of its macroscopic properties is changing over time. (**Note:** Some states that appear not to be changing may not be true equilibrium states because the changes are too slow to be observed, for example, diamond turning into graphite.)
- Properties of a system may either be independent of the amount of material present (intensive, like T and P) or proportional to the quantity of material present (extensive, like internal energy and heat capacity).
- Processes can be either irreversible (a small change in the external condition will not reverse the course of the process) or reversible (a small change in the external condition will reverse the course of the process). The latter are idealizations, often called quasi-static, and would take an infinite amount of time to occur in a real sense.

- A state function is a property whose value depends only on the current state of the system and not on the path by which that state was reached (examples include T and P). A path-dependent function is one in which the value does depend on the details of the path taken, work and heat being the most common examples.

The First Law of Thermodynamics: Internal Energy, Work, and Heat

- Work (w) is force times displacement $w = Fd$. Perhaps the most important type of work in chemistry is pressure–volume work, in which a system either expands against or is compressed by the external pressure. If the external pressure is constant, then

$$w = -P_{\text{ext}}\,\Delta V$$

- Heat (q) is the transfer of thermal energy between the system and the surroundings.
- We chose the sign convention so that $+q$ and $+w$ indicate heat is added to the system and work is done on the system.
- Heat transfer is measured by calorimetry. $q = Mc_s\Delta T$, where M is the mass of the heat-absorbing substance in the calorimeter (usually water) and c_s is the specific heat of the substance. A commercial calorimeter will have calibration factors that take into account the heat capacity of materials other than water used in its construction (for example, sample holder, walls, and so forth).
- $\Delta U = q + w$. The internal energy of a system is a state function. Although q and w are functions of the path, their sum is a state function. Heat transferred and work done must leave the energy of the thermodynamic universe unchanged.

$$q_{\text{sys}} = -q_{\text{surr}}$$

$$w_{\text{sys}} = -w_{\text{surr}}$$

$$\Delta U_{\text{sys}} = -\Delta U_{\text{surr}}$$

Heat Capacity, Enthalpy, and Calorimetry

- Heat transfer at constant volume: $\Delta U = q + w = q_{\text{v}}$. Reactions to measure ΔU are performed in a constant volume calorimeter called a bomb calorimeter.
- Heat transfer at constant pressure: enthalpy.
  Define $H = U + PV$. Then at constant pressure

$$q_{\text{p}} = \Delta(U + PV) = \Delta H$$

  Unlike constant volume processes, work can be done in constant pressure processes, so the energy change may not all show up as heat.

Illustrations of the First Law of Thermodynamics in Ideal Gas Processes

- Heat capacities of ideal monatomic gases

$$c_{\text{V}}\ (\text{ideal gas}) = 3/2\ \text{R mol}^{-1}$$

$$c_{\text{p}} = c_{\text{V}} + \text{R} = (5/2)\text{R}$$

  It takes 5/3 as much heat to increase the temperature of a gas by the same amount at constant pressure than at constant volume because some of the heat is used to pay for the work of expansion at constant pressure.

- Heat and work for ideal gases: The calculations on page 503 associated with Figure 12.10 demonstrate that the values of q and w depend on the path over which a process occurs.

Thermochemistry

- Because chemical reactions are most commonly studied at constant pressure, the heat absorbed or released in a reaction is measured as the enthalpy change of the reaction.
- Because enthalpy is a state function, enthalpy changes for any reaction of interest can be calculated by summing the enthalpy changes for a set of reactions that add up to give the reaction of interest.
- The most useful thermochemical data are tables of the standard enthalpy of formation ΔH_f° for compounds, defined as the enthalpy of formation of a compound in its standard state from the elements in their standard states at 1 atm and 298.15K.
- The change in standard state enthalpy for any reaction can be calculated from the standard state enthalpy of formation of its products and reactants as

$$\Delta H^\circ = \sum_{i=1}^{prod} n_i \Delta H_i^\circ - \sum_{j=1}^{react} n_j \Delta H_j^\circ$$

- Bond enthalpy is the enthalpy change associated with making or breaking a chemical bond. It is based on the idea that bond enthalpy, like bond energy (see Chapter 3), is approximately independent of the rest of the molecule. Average bond enthalpies are tabulated from measurements over a broad range of molecules in which the same bond appears.
- Heat transferred in phase transitions at constant pressure include $\Delta H_{\text{fus}}^\circ$ and $\Delta H_{\text{vap}}^\circ$ for melting and boiling, respectively.

Reversible Processes in Ideal Gases

- **Isothermal processes:** In this case, heat will flow (in either direction) to offset the cost of PV work, whereas T remains constant.

$$dw = -PdV$$

$$w = -\int_{V_1}^{V_2} PdV$$

- For an ideal gas, $P = nRT/V$. Because T is constant it comes outside the integral to give

$$w = -nRT\int_{V_1}^{V_2} (1/V)dV$$

$$w = -nRT\ln(V_2/V_1)$$

$$q = +nRT\ln(V_2/V_1)$$

$$\Delta U = 0$$

$$\Delta H = 0$$

- **Adiabatic processes:** No heat flows so all of the energy comes from or goes into the internal energy of the system. The key steps are:

$$q = 0, \text{ so } \Delta U = w$$

$nc_V dT = -PdV = nRTdV$ rearranging, integrating and "simplifying" gives

$$P_1V_1^\gamma = P_2V_2^\gamma, \text{ where } \gamma = c_p/c_V = 5/3 \text{ for ideal gases}$$

- The important result is that the pressure decreases faster in an adiabatic expansion than in an isothermal expansion because there is no heat to enable the expansion work and keep the pressure higher.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Give precise definitions for the terms *thermodynamic system, open system, closed system, thermodynamic state,* and *reversible* and *irreversible process* (Section 12.1).
2. Define and give examples of properties that are state functions of a system (Section 12.1).
3. Calculate the work done on an ideal gas when it is compressed reversibly (Section 12.2, Problems 1–2).
4. Give a physical interpretation to the concept of heat, and calculate the change in temperature of a given quantity of a substance from its heat capacity and the amount of heat transferred to it (Section 12.2, Problems 5–8).
5. Calculate the final temperature reached when two substances of different mass, heat capacity, and temperature are placed in thermal contact (Section 12.3, Problems 11–16).
6. Calculate the amounts of heat and work and the change in energy of an ideal gas during expansions and compressions (Section 12.4, Problems 17–22).
7. Calculate the energy and enthalpy changes for chemical reactions from the standard molar enthalpies of formation of reactants and products (Section 12.5, Problems 35–40).
8. Use bond enthalpies to estimate enthalpies of formation of gaseous compounds (Section 12.5, Problems 45–48).
9. Calculate the heat absorbed and work done by an ideal gas when it expands reversibly and either isothermally or adiabatically (Section 12.6, Problems 51–54).

KEY EQUATIONS

$w = -P_{\text{ext}}\Delta V$ **(Section 12.2)**

$q = Mc_s\Delta T$ **(Section 12.2)**

$\Delta U = q + w$ **(Section 12.2)**

$\Delta U_{\text{univ}} = \Delta U_{\text{sys}} + \Delta U_{\text{surr}} = 0$ **(Section 12.2)**

$q_V = nc_V(T_2 - T_1) = nc_V\Delta T$ **(Section 12.3)**

$q_P = nc_P\Delta T$ **(Section 12.3)**

$H = U + PV$ **(Section 12.3)**

$q_P = \Delta(U + PV) = \Delta H$ **(Section 12.3)**

$c_V = \frac{3}{2}R$ (monatomic ideal gas) **(Section 12.4)**

$c_P = c_V + R$ (any ideal gas) **(Section 12.4)**

$\Delta U = nc_V\Delta T$ (any ideal gas) **(Section 12.4)**

$\Delta H = \Delta U + \Delta(PV) = nc_V\Delta T + nR\Delta T$

$\Delta H = nc_P\Delta T$ (ideal gas) **(Section 12.4)**

$$\Delta H^\circ = \sum_{i=1}^{prod} n_i \Delta H_i^\circ - \sum_{j=1}^{react} n_j \Delta H_j^\circ$$ **(Section 12.5)**

$$w = -\int_{V_1}^{V_2} P\,dV \text{ (reversible process)}$$ **(Section 12.6)**

$$w = -nRT \ln \frac{V_2}{V_1} \text{ (ideal gas, isothermal reversible process)}$$

$$q = -w = nRT \ln \frac{V_2}{V_1} \text{ (ideal gas, isothermal reversible process)}$$ **(Section 12.6)**

$$\Delta U = 0 \text{ because } \Delta T = 0 \text{ (ideal gas, isothermal process)}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT) = 0 \text{ (ideal gas, isothermal process)}$$

$$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1} \text{ (ideal gas, reversible adiabatic process)}$$ **(Section 12.6)**

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \text{ (ideal gas, reversible adiabatic process)}$$ **(Section 12.6)**

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

The First Law of Thermodynamics: Internal Energy, Work, and Heat

1. Some nitrogen for use in synthesizing ammonia is heated slowly, maintaining the external pressure close to the internal pressure of 50.0 atm, until its volume has increased from 542 to 974 L. Calculate the work done on the nitrogen as it is heated, and express it in joules.

2. The gas mixture inside one of the cylinders of an automobile engine expands against a constant external pressure of 0.98 atm, from an initial volume of 150 mL (at the end of the compression stroke) to a final volume of 800 mL. Calculate the work done on the gas mixture during this process, and express it in joules.

3. When a ball of mass *m* is dropped through a height difference Δh, its potential energy changes by the amount $mg\,\Delta h$, where *g* is the acceleration of gravity, equal to 9.81 m s^{-2}. Suppose that when the ball hits the ground, all that energy is converted to heat, increasing the temperature of the ball. If the specific heat capacity of the material in the ball is 0.850 J K^{-1} g^{-1}, calculate the height from which the ball must be dropped to increase the temperature of the ball by 1.00°C.

4. During his honeymoon in Switzerland, James Joule is said to have used a thermometer to measure the temperature difference between the water at the top and at the bottom of a waterfall. Take the height of the waterfall to be Δh and the acceleration of gravity, *g*, to be 9.81 m s^{-2}. Assuming that all the potential energy change $mg\,\Delta h$ of a mass *m* of water is used to heat that water by the time it reaches the bottom, calculate the temperature difference between the top and the bottom of a waterfall 100 meters high. Take the specific heat capacity of water to be 4.18 J K^{-1} g^{-1}.

5. The specific heat capacities of Li(*s*), Na(*s*), K(*s*), Rb(*s*), and Cs(*s*) at 25°C are 3.57, 1.23, 0.756, 0.363, and 0.242 J K^{-1} g^{-1}, respectively. Compute the molar heat capacities of these elements and identify any periodic trend. If there is a trend, use it to predict the molar heat capacity of francium, Fr(*s*).

6. The specific heat capacities of $F_2(g)$, $Cl_2(g)$, $Br_2(g)$, and $I_2(g)$ are 0.824, 0.478, 0.225, and 0.145 J K^{-1} g^{-1}, respectively. Compute the molar heat capacities of these elements and identify any periodic trend. If there is a trend, use it to predict the molar heat capacity of astatine, $At_2(g)$.

7. The specific heat capacities of the metals nickel, zinc, rhodium, tungsten, gold, and uranium at 25°C are 0.444, 0.388, 0.243, 0.132, 0.129, and 0.116 J K^{-1} g^{-1}, respectively. Calculate the molar heat capacities of these six metals. Note how closely the molar heat capacities for these metals, which were selected at random, cluster about a value of 25 J K^{-1} mol^{-1}. The rule of Dulong and Petit states that the molar heat capacities of the metallic elements are approximately 25 J K^{-1} mol^{-1}.

8. Use the empirical rule of Dulong and Petit stated in Problem 7 to estimate the specific heat capacities of vanadium, gallium, and silver.

9. A chemical system is sealed in a strong, rigid container at room temperature, and then heated vigorously.
   (a) State whether ΔU, *q*, and *w* of the system are positive, negative, or zero during the heating process.
   (b) Next, the container is cooled to its original temperature. Determine the signs of ΔU, *q*, and *w* for the cooling process.
   (c) Designate heating as step 1 and cooling as step 2. Determine the signs of $(\Delta U_1 + \Delta U_2)$, $(q_1 + q_2)$, and $(w_1 + w_2)$, if possible.

10. A battery harnesses a chemical reaction to extract energy in the form of useful electrical work.
   (a) A certain battery runs a toy truck and becomes partially discharged. In the process, it performs a total of 117.0 J

of work on its immediate surroundings. It also gives off 3.0 J of heat, which the surroundings absorb. No other work or heat is exchanged with the surroundings. Compute q, w, and ΔU of the battery, making sure each quantity has the proper sign.

(b) The same battery is now recharged exactly to its original condition. This requires 210.0 J of electrical work from an outside generator. Determine q for the battery in this process. Explain why q has the sign that it does.

Heat Capacity, Enthalpy, and Calorimetry

11. Suppose 61.0 g hot metal, which is initially at 120.0°C, is plunged into 100.0 g water that is initially at 20.00°C. The metal cools down and the water heats up until they reach a common temperature of 26.39°C. Calculate the specific heat capacity of the metal, using 4.18 $\text{J K}^{-1}\text{ g}^{-1}$ as the specific heat capacity of the water.

12. A piece of zinc at 20.0°C that weighs 60.0 g is dropped into 200.0 g water at 100.0°C. The specific heat capacity of zinc is 0.389 $\text{J K}^{-1}\text{ g}^{-1}$, and that of water near 100°C is 4.22 $\text{J K}^{-1}\text{ g}^{-1}$. Calculate the final temperature reached by the zinc and the water.

13. Very early in the study of the nature of heat it was observed that if two bodies of equal mass but different temperatures are placed in thermal contact, their specific heat capacities depend inversely on the change in temperature each undergoes on reaching its final temperature. Write a mathematical equation in modern notation to express this fact.

14. Iron pellets with total mass 17.0 g at a temperature of 92.0°C are mixed in an insulated container with 17.0 g water at a temperature of 20.0°C. The specific heat capacity of water is 10 times greater than that of iron. What is the final temperature inside the container?

15. In their *Memoir on Heat,* published in 1783, Lavoisier and Laplace reported, "The heat necessary to melt ice is equal to three quarters of the heat that can raise the same mass of water from the temperature of the melting ice to that of boiling water" (English translation). Use this 18th-century observation to compute the amount of heat (in joules) needed to melt 1.00 g ice. Assume that heating 1.00 g water requires 4.18 J of heat for each 1.00°C throughout the range from 0°C to 100°C.

16. Galen, the great physician of antiquity, suggested scaling temperature from a reference point defined by mixing equal masses of ice and boiling water in an insulated container. Imagine that this is done with the ice at 0.00°C and the water at 100.0°C. Assume that the heat capacity of the container is negligible, and that it takes 333.4 J of heat to melt 1.000 g ice at 0.00°C to water at 0.00°C. Compute Galen's reference temperature in degrees Celsius.

Illustrations of the First Law of Thermodynamics in Ideal Gas Processes

17. If 0.500 mol neon at 1.00 atm and 273 K expands against a constant external pressure of 0.100 atm until the gas pressure reaches 0.200 atm and the temperature reaches 210 K, calculate the work done on the gas, the internal energy change, and the heat absorbed by the gas.

18. Hydrogen behaves as an ideal gas at temperatures greater than 200 K and at pressures less than 50 atm. Suppose 6.00 mol hydrogen is initially contained in a 100-L vessel at a pressure of 2.00 atm. The average molar heat capacity of hydrogen at constant pressure, c_P, is 29.3 $\text{J K}^{-1}\text{ mol}^{-1}$ in the temperature range of this problem. The gas is cooled reversibly at constant pressure from its initial state to a volume of 50.0 L. Calculate the following quantities for this process.

(a) Temperature of the gas in the final state, T_2
(b) Work done on the gas, w, in joules
(c) Internal energy change of the gas, ΔU, in joules
(d) Heat absorbed by the gas, q, in joules

19. Suppose 2.00 mol of an ideal, monatomic gas is initially at a pressure of 3.00 atm and a temperature $T = 350$ K. It is expanded *irreversibly* and *adiabatically* ($q = 0$) against a constant external pressure of 1.00 atm until the volume has doubled.

(a) Calculate the final volume.
(b) Calculate w, q, and ΔU for this process, in joules.
(c) Calculate the final temperature of the gas.

20. Consider the free, isothermal (constant T) expansion of an ideal gas. "Free" means that the external force is zero, perhaps because a stopcock has been opened and the gas is allowed to expand into a vacuum. Calculate ΔU for this irreversible process. Show that $q = 0$, so that the expansion is also adiabatic ($q = 0$) for an ideal gas. This is analogous to a classic experiment first performed by Joule.

21. If 6.00 mol argon in a 100-L vessel initially at 300 K is compressed adiabatically ($q = 0$) and irreversibly until a final temperature of 450 K is reached, calculate the energy change of the gas, the heat added to the gas, and the work done on the gas.

22. A gas expands against a constant external pressure of 2.00 atm until its volume has increased from 6.00 to 10.00 L. During this process, it absorbs 500 J of heat from the surroundings.

(a) Calculate the energy change of the gas, ΔU.
(b) Calculate the work, w, done on the gas in an irreversible adiabatic ($q = 0$) process connecting the same initial and final states.

Thermochemistry

23. For each of the following reactions, the enthalpy change written is that measured when the numbers of moles of reactants and products taking part in the reaction are as given by their coefficients in the equation. Calculate the enthalpy change when 1.00 *gram* of the underlined substance is consumed or produced.

(a) $4\text{ Na}(s) + \text{O}_2(g) \longrightarrow \underline{2\text{ Na}_2\text{O}(s)}$ $\quad \Delta H = -828$ kJ
(b) $\text{CaMg(CO}_3)_2(s) \longrightarrow \underline{\text{CaO}(s)} + \underline{\text{MgO}(s)} + 2\text{ CO}_2(g)$ $\quad \Delta H = +302$ kJ
(c) $\text{H}_2(g) + 2\ \underline{\text{CO}(g)} \longrightarrow \text{H}_2\text{O}_2(\ell) + 2\text{ C}(s)$ $\quad \Delta H = +33.3$ kJ

24. For each of the following reactions, the enthalpy change given is that measured when the numbers of moles of reactants and products taking part in the reaction are as given by their coefficients in the equation. Calculate the enthalpy change when 1.00 *gram* of the underlined substance is consumed or produced.

(a) $Ca(s) + \underline{Br_2(\ell)} \longrightarrow CaBr_2(s) \qquad \Delta H = -683\ \text{kJ}$

(b) $6\ Fe_2O_3(s) \longrightarrow 4\ \underline{Fe_3O_4(s)} + O_2(g) \qquad \Delta H = +472\ \text{kJ}$

(c) $2\ \underline{NaHSO_4(s)} \longrightarrow 2\ NaOH(s) + 2\ SO_2(g) + O_2(g) \qquad \Delta H = +806\ \text{kJ}$

25. Liquid bromine dissolves readily in aqueous NaOH:

$$Br_2(\ell) + 2\ NaOH(aq) \rightarrow NaBr(aq) + NaOBr(aq) + H_2O(\ell)$$

Suppose 2.88×10^{-6} mol of $Br_2(\ell)$ is sealed in a glass capsule that is then immersed in a solution containing excess $NaOH(aq)$. The capsule is broken, the mixture is stirred, and a measured 121.3 J of heat evolves. In a separate experiment, simply breaking an empty capsule and stirring the solution in the same way evolves 2.34 J of heat. Compute the heat evolved as 1.00 mol $Br_2(\ell)$ dissolves in excess $NaOH(aq)$.

26. A chemist mixes 1.00 g $CuCl_2$ with an excess of $(NH_4)_2HPO_4$ in dilute aqueous solution. He measures the evolution of 670 J of heat as the two substances react to give $Cu_3(PO_4)_2(s)$. Compute the ΔH that would result from the reaction of 1.00 mol $CuCl_2$ with an excess of $(NH_4)_2HPO_4$.

27. Calculate the enthalpy change when 2.38 g carbon monoxide (CO) vaporizes at its normal boiling point. Use data from Table 12.2.

28. Molten sodium chloride is used for making elemental sodium and chlorine. Suppose the electrical power to a vat containing 56.2 kg molten sodium chloride is cut off and the salt crystallizes (without changing its temperature). Calculate the enthalpy change, using data from Table 12.2.

29. Suppose an ice cube weighing 36.0 g at a temperature of −10°C is placed in 360 g water at a temperature of 20°C. Calculate the temperature after thermal equilibrium is reached, assuming no heat loss to the surroundings. The enthalpy of fusion of ice is $\Delta H_{\text{fus}} = 6.007\ \text{kJ mol}^{-1}$, and the molar heat capacities c_P of ice and water are 38 and $75\ \text{J K}^{-1}\ \text{mol}^{-1}$, respectively.

30. You have a supply of ice at 0.0°C and a glass containing 150 g water at 25°C. The enthalpy of fusion for ice is $\Delta H_{\text{fus}} = 333\ \text{J g}^{-1}$, and the specific heat capacity of water is $4.18\ \text{J K}^{-1}\ \text{g}^{-1}$. How many grams of ice must be added to the glass (and melted) to reduce the temperature of the water to 0°C?

31. The measured enthalpy change for burning ketene (CH_2CO)

$$CH_2CO(g) + 2\ O_2(g) \longrightarrow 2\ CO_2(g) + H_2O(g)$$

is $\Delta H_1 = -981.1$ kJ at 25°C. The enthalpy change for burning methane

$$CH_4(g) + 2\ O_2(g) \longrightarrow CO_2(g) + 2\ H_2O(g)$$

is $\Delta H_2 = -802.3$ kJ at 25°C. Calculate the enthalpy change at 25°C for the reaction

$$2\ CH_4(g) + 2\ O_2(g) \longrightarrow CH_2CO(g) + 3\ H_2O(g)$$

32. Given the following two reactions and corresponding enthalpy changes,

$$CO(g) + SiO_2(s) \longrightarrow SiO(g) + CO_2(g) \qquad \Delta H = +520.9\ \text{kJ}$$

$$8\ CO_2(g) + Si_3N_4(s) \longrightarrow 3\ SiO_2(s) + 2\ N_2O(g) + 8\ CO(g) \qquad \Delta H = +461.05\ \text{kJ}$$

compute the ΔH of the reaction

$$5\ CO_2(g) + Si_3N_4(s) \longrightarrow 3\ SiO(g) + 2\ N_2O(g) + 5\ CO(g)$$

33. The enthalpy change to make diamond from graphite is $1.88\ \text{kJ mol}^{-1}$. Which gives off more heat when burned—a pound of diamonds or a pound of graphite? Explain.

34. The enthalpy change of combustion of monoclinic sulfur to $SO_2(g)$ is $-9.376\ \text{kJ g}^{-1}$. Under the same conditions, the rhombic form of sulfur has an enthalpy change of combustion to $SO_2(g)$ of $-9.293\ \text{kJ g}^{-1}$. Compute the ΔH of the reaction

$$S(\text{monoclinic}) \longrightarrow S(\text{rhombic})$$

per gram of sulfur reacting.

35. Calculate the standard enthalpy change $\Delta H°$ at 25°C for the reaction

$$N_2H_4(\ell) + 3\ O_2(g) \longrightarrow 2\ NO_2(g) + 2\ H_2O(\ell)$$

using the standard enthalpies of formation ($\Delta H°_f$) of reactants and products at 25°C from Appendix D.

36. Using the data in Appendix D, calculate $\Delta H°$ for each of the following processes:

(a) $2\ NO(g) + O_2(g) \longrightarrow 2\ NO_2(g)$

(b) $C(s) + CO_2(g) \longrightarrow 2\ CO(g)$

(c) $2\ NH_3(g) + \frac{7}{2}\ O_2(g) \longrightarrow 2\ NO_2(g) + 3\ H_2O(g)$

(d) $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$

37. Zinc is commonly found in nature in the form of the mineral sphalerite (ZnS). A step in the smelting of zinc is the roasting of sphalerite with oxygen to produce zinc oxide:

$$2\ ZnS(s) + 3\ O_2(g) \longrightarrow 2\ ZnO(s) + 2\ SO_2(g)$$

(a) Calculate the standard enthalpy change $\Delta H°$ for this reaction, using data from Appendix D.

(b) Calculate the heat absorbed when 3.00 metric tons (1 metric ton = 10^3 kg) of sphalerite is roasted under constant-pressure conditions.

38. The thermite process (see Fig. 12.11) is used for welding railway track together. In this reaction, aluminum reduces iron(III) oxide to metallic iron:

$$2\ Al(s) + Fe_2O_3(s) \longrightarrow 2\ Fe(s) + Al_2O_3(s)$$

Igniting a small charge of barium peroxide mixed with aluminum triggers the reaction of a mixture of aluminum powder and iron(III) oxide; the molten iron produced flows into the space between the steel rails that are to be joined.

(a) Calculate the standard enthalpy change $\Delta H°$ for this reaction, using data from Appendix D.

(b) Calculate the heat given off when 3.21 g iron(III) oxide is reduced by aluminum at constant pressure.

39. The dissolution of calcium chloride in water

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2\ Cl^-(aq)$$

is used in first-aid hot packs. In these packs, an inner pouch containing the salt is broken, allowing the salt to dissolve in the surrounding water.

(a) Calculate the standard enthalpy change $\Delta H°$ for this reaction, using data from Appendix D.

(b) Suppose 20.0 g $CaCl_2$ is dissolved in 0.100 L water at 20.0°C. Calculate the temperature reached by the solution, assuming it to be an ideal solution with a heat capacity close to that of 100 g pure water (418 J K^{-1}).

40. Ammonium nitrate dissolves in water according to the reaction

$$NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$$

(a) Calculate the standard enthalpy change $\Delta H°$ for this reaction, using data from Appendix D.

(b) Suppose 15.0 g NH_4NO_3 is dissolved in 0.100 L water at 20.0°C. Calculate the temperature reached by the solution, assuming it to be an ideal solution with a heat capacity close to that of 100 g pure water (418 J K^{-1}).

(c) From a comparison with the results of Problem 39, can you suggest a practical application of this dissolution reaction?

41. The standard enthalpy change of combustion [to $CO_2(g)$ and $H_2O(\ell)$] at 25°C of the organic liquid cyclohexane, $C_6H_{12}(\ell)$, is -3923.7 kJ mol^{-1}. Determine the $\Delta H_f°$ of $C_6H_{12}(\ell)$. Use data from Appendix D.

42. The standard enthalpy change of combustion [to $CO_2(g)$ and $H_2O(\ell)$] at 25°C of the organic liquid cyclohexane, $C_6H_{10}(\ell)$, is -3731.7 kJ mol^{-1}. Determine the $\Delta H_f°$ of $C_6H_{10}(\ell)$.

43. A sample of pure solid naphthalene ($C_{10}H_8$) weighing 0.6410 g is burned completely with oxygen to $CO_2(g)$ and $H_2O(\ell)$ in a constant-volume calorimeter at 25°C. The amount of heat evolved is observed to be 25.79 kJ.

(a) Write and balance the chemical equation for the combustion reaction.

(b) Calculate the standard change in internal energy ($\Delta U°$) for the combustion of 1.000 mol naphthalene to $CO_2(g)$ and $H_2O(\ell)$.

(c) Calculate the standard enthalpy change ($\Delta H°$) for the same reaction as in part (b).

(d) Calculate the standard enthalpy of formation per mole of naphthalene, using data for the standard enthalpies of formation of $CO_2(g)$ and $H_2O(\ell)$ from Appendix D.

44. A sample of solid benzoic acid (C_6H_5COOH) that weighs 0.800 g is burned in an excess of oxygen to $CO_2(g)$ and $H_2O(\ell)$ in a constant-volume calorimeter at 25°C. The temperature increase is observed to be 2.15°C. The heat capacity of the calorimeter and its contents is known to be 9382 J K^{-1}.

(a) Write and balance the equation for the combustion of benzoic acid.

(b) Calculate the standard change in internal energy ($\Delta U°$) for the combustion of 1.000 mol benzoic acid to $CO_2(g)$ and $H_2O(\ell)$ at 25°C.

(c) Calculate the standard enthalpy change ($\Delta H°$) for the same reaction as in part (b).

(d) Calculate the standard enthalpy of formation per mole of benzoic acid, using data for the standard enthalpies of formation of $CO_2(g)$ and $H_2O(\ell)$ from Appendix D.

45. A second CFC used as a refrigerant and in aerosols (besides that discussed in Example 12.8) is CCl_3F. Use the atomization enthalpies and average bond enthalpies from Table 12.3 to estimate the standard enthalpy of formation ($\Delta H_f°$) of this compound in the gas phase.

46. The compound CF_3CHCl_2 (with a C—C bond) has been proposed as a substitute for CCl_3F and CCl_2F_2 because it decomposes more quickly in the atmosphere and is much less liable to reduce the concentration of ozone in the stratosphere. Use the atomization enthalpies and average bond enthalpies from Table 12.3 to estimate the standard enthalpy of formation ($\Delta H_f°$) of CF_3CHCl_2 in the gas phase.

47. Propane has the structure $H_3C{-}CH_2{-}CH_3$. Use average bond enthalpies from Table 12.3 to estimate the change in enthalpy $\Delta H°$ for the reaction

$$C_3H_8(g) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(g)$$

48. Use average bond enthalpies from Table 12.3 to estimate the change in enthalpy $\Delta H°$ for the reaction

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

Refer to the molecular structures on page 86.

49. The following reaction

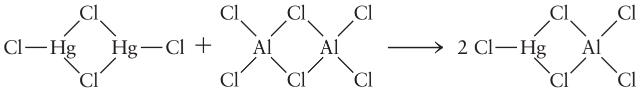
$$BBr_3(g) + BCl_3(g) \longrightarrow BBr_2Cl(g) + BCl_2Br(g)$$

has a ΔH close to zero. Sketch the Lewis structures of the four compounds, and explain why ΔH is so small.

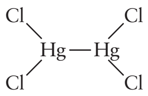
50. At 381 K, the following reaction takes place:

$$Hg_2Cl_4(g) + Al_2Cl_6(g) \longrightarrow 2\ HgAlCl_5(g) \qquad \Delta H = +10\ \text{kJ}$$

(a) Offer an explanation for the very small ΔH for this reaction for the known structures of the compounds



(b) Explain why the small ΔH in this reaction is evidence against



as the structure of $Hg_2Cl_4(g)$.

Reversible Processes in Ideal Gases

51. If 2.00 mol of an ideal gas at 25°C expands isothermally and reversibly from 9.00 to 36.00 L, calculate the work done on the gas and the heat absorbed by the gas in the process. What are the changes in energy (ΔU) and in enthalpy (ΔH) of the gas in the process?

52. If 54.0 g argon at 400 K is compressed isothermally and reversibly from a pressure of 1.50 to 4.00 atm, calculate the work done on the gas and the heat absorbed by gas in the process. What are the changes in energy (ΔU) and in enthalpy (ΔH) of the gas?

53. Suppose 2.00 mol of a monatomic ideal gas ($c_V = \frac{3}{2}R$) is expanded adiabatically and reversibly from a temperature $T = 300$ K, where the volume of the system is 20.0 L, to a volume of 60.0 L. Calculate the final temperature of the gas, the work done on the gas, and the energy and enthalpy changes.

54. Suppose 2.00 mol of an ideal gas is contained in a heat-insulated cylinder with a moveable frictionless piston. Initially, the gas is at 1.00 atm and 0°C. The gas is compressed reversibly to 2.00 atm. The molar heat capacity at constant pressure, c_P, equals 29.3 J K^{-1} mol^{-1}. Calculate the final temperature of the gas, the change in its internal energy, ΔU, and the work done on the gas.

ADDITIONAL PROBLEMS

55. At one time it was thought that the molar mass of indium was near 76 g mol^{-1}. By referring to the law of Dulong and Petit (see Problem 7), show how the measured specific heat of metallic indium, 0.233 J K^{-1} g^{-1}, makes this value unlikely.

56. The following table shows how the specific heat at constant pressure of liquid helium changes with temperature. Note the sharp increase over this temperature range:

Temperature (K):

1.80	1.85	1.90	1.95	2.00	2.05	2.10	2.15

c_s (J K^{-1} g^{-1}):

2.81	3.26	3.79	4.42	5.18	6.16	7.51	9.35

Estimate how much heat it takes at constant pressure to increase the temperature of 1.00 g He(ℓ) from 1.8 to 2.15 K. (*Hint:* For each temperature interval of 0.05 K, take the average, c_s, as the sum of the values at the ends of the interval divided by 2.)

57. Imagine that 2.00 mol argon, confined by a moveable, frictionless piston in a cylinder at a pressure of 1.00 atm and a temperature of 398 K, is cooled to 298 K. Argon gas may be considered ideal, and its molar heat capacity at constant pressure is $c_P = (5/2)R$, where $R = 8.315$ J K^{-1} mol^{-1}. Calculate:

(a) The work done on the system, w
(b) The heat absorbed by the system, q
(c) The energy change of the system, ΔU
(d) The enthalpy change of the system, ΔH

58. Suppose 1.00 mol ice at −30°C is heated at atmospheric pressure until it is converted to steam at 140°C. Calculate q, w, ΔH, and ΔU for this process. For ice, water, and steam, c_P is 38, 75, and 36 J K^{-1} mol^{-1}, respectively, and can be taken to be approximately independent of temperature. ΔH_{fus} for ice is 6.007 kJ mol^{-1}, and ΔH_{vap} for water is 40.66 kJ mol^{-1}. Use the ideal gas law for steam, and assume that the volume of 1 mol ice or water is negligible relative to that of 1 mol steam.

59. The gas inside a cylinder expands against a constant external pressure of 1.00 atm from a volume of 5.00 L to a volume of 13.00 L. In doing so, it turns a paddle immersed in 1.00 L water. Calculate the temperature increase of the water, assuming no loss of heat to the surroundings or frictional losses in the mechanism. Take the density of water to be 1.00 g cm^{-3} and its specific heat to be 4.18 J K^{-1} g^{-1}.

60. Suppose 1.000 mol argon (assumed to be an ideal gas) is confined in a strong, rigid container of volume 22.41 L at 273.15 K. The system is heated until 3.000 kJ (3000 J) of heat has been added. The molar heat capacity of the gas does not change during the heating and equals 12.47 J K^{-1} mol^{-1}.

(a) Calculate the original pressure inside the vessel (in atmospheres).
(b) Determine q for the system during the heating process.
(c) Determine w for the system during the heating process.
(d) Compute the temperature of the gas after the heating, in degrees Celsius. Assume the container has zero heat capacity.
(e) Compute the pressure (in atmospheres) inside the vessel after the heating.
(f) Compute ΔU of the gas during the heating process.
(g) Compute ΔH of the gas during the heating process.
(h) The correct answer to part (g) exceeds 3.000 kJ. The increase in enthalpy (which at one time was misleadingly called the "heat content") in this system exceeds the amount of heat actually added. Why is this not a violation of the law of conservation of energy?

61. When glucose, a sugar, reacts fully with oxygen, carbon dioxide and water are produced:

$$C_6H_{12}O_6(s) + 6\ O_2(g) \longrightarrow 6\ CO_2(g) + 6\ H_2O(\ell) \qquad \Delta H° = -2820 \text{ kJ}$$

Suppose a person weighing 50 kg (mostly water, with specific heat capacity 4.18 J K^{-1} g^{-1}) eats a candy bar containing 14.3 g glucose. If all the glucose reacted with oxygen and the heat produced were used entirely to increase the person's body temperature, what temperature increase would result? (In fact, most of the heat produced is lost to the surroundings before such a temperature increase occurs.)

62. In walking 1 km, you use about 100 kJ of energy. This energy comes from the oxidation of foods, which is about 30% efficient. How much energy do you save by walking 1 km instead of driving a car that gets 8.0 km L^{-1} gasoline (19 miles/gal)? The density of gasoline is 0.68 g cm^{-3} and its enthalpy of combustion is −48 kJ g^{-1}.

63. Liquid helium and liquid nitrogen are both used as coolants; He(ℓ) boils at 4.21 K, and $N_2(\ell)$ boils at 77.35 K. The specific heat of liquid helium near its boiling point is 4.25 J K^{-1} g^{-1}, and the specific heat of liquid nitrogen near *its* boiling point is 1.95 J K^{-1} g^{-1}. The enthalpy of vaporization of He(ℓ) is 25.1 J g^{-1}, and the enthalpy of vaporization of $N_2(\ell)$ is 200.3 J g^{-1} (these data are calculated from the values in Appendix F). Discuss which liquid is the better coolant (on a per-gram basis) *near* its boiling point and which is better *at* its boiling point.

64. When 1.00 g potassium chlorate ($KClO_3$) is dissolved in 50.0 g water in a Styrofoam calorimeter of negligible heat capacity, the temperature decreases from 25.00°C to 23.36°C. Calculate q for the water and $\Delta H°$ for the process.

$$KClO_3(s) \longrightarrow K^+(aq) + ClO_3^-(aq)$$

The specific heat of water is 4.184 J K^{-1} g^{-1}.

65. The enthalpy of combustion and the standard enthalpy of formation of a fuel can be determined by measuring the temperature change in a calorimeter when a weighed amount of the fuel is burned in oxygen.

(a) Write a balanced chemical equation for the combustion of isooctane, $C_8H_{18}(\ell)$, to $CO_2(g)$ and $H_2O(\ell)$. Isooctane is a component of gasoline and is used as a reference standard in determining the "octane rating" of a fuel mixture.

(b) Suppose 0.542 g isooctane is placed in a fixed-volume (bomb) calorimeter, which contains 750 g water, initially at 20.450°C, surrounding the reaction compartment. The heat capacity of the calorimeter itself (excluding the water) has been measured to be 48 J K^{-1} in a separate calibration. After the combustion of the isooctane is complete, the water temperature is measured to be 28.670°C. Taking the specific heat of water to be 4.184 J K^{-1} g^{-1}, calculate ΔE for the combustion of 0.542 g isooctane.

(c) Calculate ΔU for the combustion of 1 mol isooctane.

(d) Calculate ΔH for the combustion of 1 mol isooctane.

(e) Calculate $\Delta H°_f$ for the isooctane.

66. The enthalpy change to form 1 mol $Hg_2Br_2(s)$ from the elements at 25°C is −206.77 kJ mol^{-1}, and that of $HgBr(g)$ is 96.23 kJ mol^{-1}. Compute the enthalpy change for the decomposition of 1 mol $Hg_2Br_2(s)$ to 2 mol $HgBr(g)$:

$$Hg_2Br_2(s) \longrightarrow 2\ HgBr(g)$$

* **67.** The gas most commonly used in welding is acetylene, $C_2H_2(g)$. When acetylene is burned in oxygen, the reaction is

$$C_2H_2(g) + \tfrac{5}{2}\ O_2(g) \longrightarrow 2\ CO_2(g) + H_2O(g)$$

(a) Using data from Appendix D, calculate $\Delta H°$ for this reaction.

(b) Calculate the total heat capacity of 2.00 mol $CO_2(g)$ and 1.00 mol $H_2O(g)$, using $c_P(CO_2(g))$ = 37 J K^{-1} mol^{-1} and $c_P(H_2O(g))$ = 36 J K^{-1} mol^{-1}.

(c) When this reaction is performed in an open flame, almost all the heat produced in part (a) goes to increase the temperature of the products. Calculate the maximum flame temperature that is attainable in an open flame burning acetylene in oxygen. The actual flame temperature would be lower than this because heat is lost to the surroundings.

* **68.** The enthalpy of reaction changes somewhat with temperature. Suppose we wish to calculate ΔH for a reaction at a temperature T that is different from 298 K. To do this, we can replace the direct reaction at T with a three-step process. In the first step, the temperature of the reactants is changed from T to 298 K. ΔH for this step can be calculated from the molar heat capacities of the reactants, which are assumed to be independent of temperature. In the second step, the reaction is conducted at 298 K with an enthalpy change $\Delta H°$. In the third step, the temperature of the products is changed from 298 K to T. The sum of these three enthalpy changes is ΔH for the reaction at temperature T.

An important process contributing to air pollution is the following chemical reaction

$$SO_2(g) + \tfrac{1}{2}\ O_2(g) \longrightarrow SO_3(g)$$

For $SO_2(g)$, the heat capacity c_P is 39.9, for $O_2(g)$ it is 29.4, and for $SO_3(g)$ it is 50.7 J K^{-1} mol^{-1}. Calculate ΔH for the preceding reaction at 500 K, using the enthalpies of formation at 298.15 K from Appendix D.

69. At the top of the compression stroke in one of the cylinders of an automobile engine (that is, at the minimum gas volume), the volume of the gas-air mixture is 150 mL, the temperature is 600 K, and the pressure is 12.0 atm. The ratio of the number of moles of octane vapor to the number of moles of air in the combustion mixture is 1.00:80.0. What is the maximum temperature attained in the gas if octane burns explosively before the power stroke of the piston (gas expansion) begins? The gases may be considered to be ideal, and their heat capacities at constant pressure (assumed to be temperature-independent) are

$$c_P(C_8H_{18}(g)) = 327\ J\ K^{-1}\ mol^{-1}$$
$$c_P(O_2(g)) = 35.2\ J\ K^{-1}\ mol^{-1}$$
$$c_P(N_2(g)) = 29.8\ J\ K^{-1}\ mol^{-1}$$
$$c_P(CO_2(g)) = 45.5\ J\ K^{-1}\ mol^{-1}$$
$$c_P(H_2O(g)) = 38.9\ J\ K^{-1}\ mol^{-1}$$

The enthalpy of formation of $C_8H_{18}(g)$ at 600 K is −57.4 kJ mol^{-1}.

70. Initially, 46.0 g oxygen is at a pressure of 1.00 atm and a temperature of 400 K. It expands adiabatically and reversibly until the pressure is reduced to 0.60 atm, and it is then compressed isothermally and reversibly until the volume returns to its original value. Calculate the final pressure and temperature of the oxygen, the work done and heat added to the oxygen in this process, and the energy change ΔU. Take $c_P(O_2)$ = 29.4 J K^{-1} mol^{-1}.

71. A young chemist buys a "one-lung" motorcycle but, before learning how to drive it, wants to understand the processes that occur in its engine. The manual says the cylinder has a radius of 5.00 cm, a piston stroke of 12.00 cm, and a (volume) compression ratio of 8:1. If a mixture of gasoline vapor (taken to be C_8H_{18}) and air in mole ratio 1:62.5 is drawn into the cylinder at 80°C and 1.00 atm, calculate:

(a) The temperature of the compressed gases just before the spark plug ignites them. (Assume the gases are ideal, the compression is adiabatic, and the average heat capacity of the mixture of gasoline vapor and air is c_P = 35 J K^{-1} mol^{-1}.)

(b) The volume of the compressed gases just before ignition.

(c) The pressure of the compressed gases just before ignition.

(d) The maximum temperature of the combustion products, assuming combustion is completed before the piston begins its downstroke. Take $\Delta H_f^\circ(C_8H_{18})$ = −57.4 kJ mol^{-1}.

(e) The temperature of the exhaust gases, assuming the expansion stroke to be adiabatic.

72. Nitromethane, CH_3NO_2, is a good fuel. It is a liquid at ordinary temperatures. When the liquid is burned, the reaction involved is chiefly

$$2\ CH_3NO_2(\ell) + \tfrac{3}{2}\ O_2(g) \longrightarrow 2\ CO_2(g) + N_2(g) + 3\ H_2O(g)$$

The standard enthalpy of formation of liquid nitromethane at 25°C is -112 kJ mol^{-1}; other relevant values can be found in Appendix D.

(a) Calculate the enthalpy change in the burning of 1 mol liquid nitromethane to form gaseous products at 25°C. State explicitly whether the reaction is endothermic or exothermic.

(b) Would more or less heat be evolved if *gaseous* nitromethane were burned under the same conditions? Indicate what additional information (if any) you would need to calculate the exact amount of heat, and show just how you would use this information.

73. Dry air containing a small amount of CO was passed through a tube containing a catalyst for the oxidation of CO to CO_2. Because of the heat evolved in this oxidation, the temperature of the air increased by 3.2 K. Calculate the weight percentage of CO in the sample of air. Assume that the specific heat at constant pressure for air is 1.01 J K^{-1} g^{-1}.

74. When 1 mol isobutane, a gas with formula C_4H_8, is burned at 25°C and 1 atm to form CO_2 and gaseous water, the enthalpy change is -2528 kJ.

(a) Calculate, with the aid of any information needed from Table D-4 in Appendix D, the standard enthalpy of formation of isobutane.

(b) Suppose that 0.50 mol isobutane is burned adiabatically at constant pressure in the presence of an excess of oxygen, with 5.0 mol oxygen left at the end of the reaction. The heat capacity of the reaction vessel is 700 J K^{-1}, and pertinent molar heat capacities (in joules per kelvin per mole) are $CO_2(g)$, 37; $H_2O(g)$, 34; $O_2(g)$, 29. What is the approximate final temperature of this system (including the reaction vessel)?

75. Find the maximum possible temperature that may be reached when 0.050 mol $Ca(OH)_2(s)$ is allowed to react with 1.0 L of a 1.0-M HCl solution, both initially at 25°C. Assume that the final volume of the solution is 1.0 L, and that the specific heat at constant pressure of the solution is constant and equal to that of water, 4.18 J K^{-1} g^{-1}.

CUMULATIVE PROBLEMS

76. Suppose 32.1 g $ClF_3(g)$ and 17.3 g $Li(s)$ are mixed and allowed to react at atmospheric pressure and 25°C until one of the reactants is used up, producing $LiCl(s)$ and $LiF(s)$. Calculate the amount of heat evolved.

77. Calculate ΔH_f° and ΔU_f° for the formation of silane, $SiH_4(g)$, from its elements at 298 K, if 250 cm^3 of the gaseous compound at $T = 298$ K and $P = 0.658$ atm is burned in a constant-volume gas calorimeter in an excess of oxygen and causes the evolution of 9.757 kJ of heat. The combustion reaction is

$$SiH_4(g) + 2\ O_2(g) \longrightarrow SiO_2(s,\ \text{quartz}) + 2\ H_2O(\ell)$$

and the formation of silane from its elements is

$$Si(s) + 2\ H_2(g) \longrightarrow SiH_4(g)$$

78. (a) Draw Lewis diagrams for O_2, CO_2, H_2O, CH_4, C_8H_{18}, and C_2H_5OH. In C_8H_{18}, the eight carbon atoms form a chain with single bonds; in C_2H_5OH, the two carbon atoms are bonded to one another. Using average bond enthalpies from Table 12.3, compute the enthalpy change in each of the following reactions, if 1 mol of each carbon compound is burned, and all reactants and products are in the gas phase.

(b) $CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$ (burning methane, or natural gas)

(c) $C_8H_{18} + \frac{25}{2}\ O_2 \longrightarrow 8\ CO_2 + 9\ H_2O$ (burning octane, in gasoline)

(d) $C_2H_5OH + 3\ O_2 \longrightarrow 2\ CO_2 + 3\ H_2O$ (burning ethanol, in gasohol)

79. By considering the nature of the intermolecular forces in each case, rank the following substances from smallest to largest enthalpy of vaporization: KBr, Ar, NH_3, and He. Explain your reasoning.

80. A supersonic nozzle is a cone-shaped object with a small hole in the end through which a gas is forced. As it moves through the nozzle opening, the gas expands in a manner that can be approximated as reversible and adiabatic. Such nozzles are used in molecular beams (see Section 17.4) and in supersonic aircraft engines to provide thrust, because as the gas cools, its random thermal energy is converted into directed motion of the molecules with average velocity v. Little thermodynamic work is done because the external pressure is low; thus, the net effect is to convert thermal energy to net translational motion of the gas molecules. Suppose the gas in the nozzle is helium; its pressure is 50 atm and its temperature is 400 K before it begins its expansion.

(a) What are the average speed and the average velocity of the molecules *before* the expansion?

(b) What will be the temperature of the gas after its pressure has decreased to 1.0 atm in the expansion?

(c) What is the average velocity of the molecules at this point in the expansion?

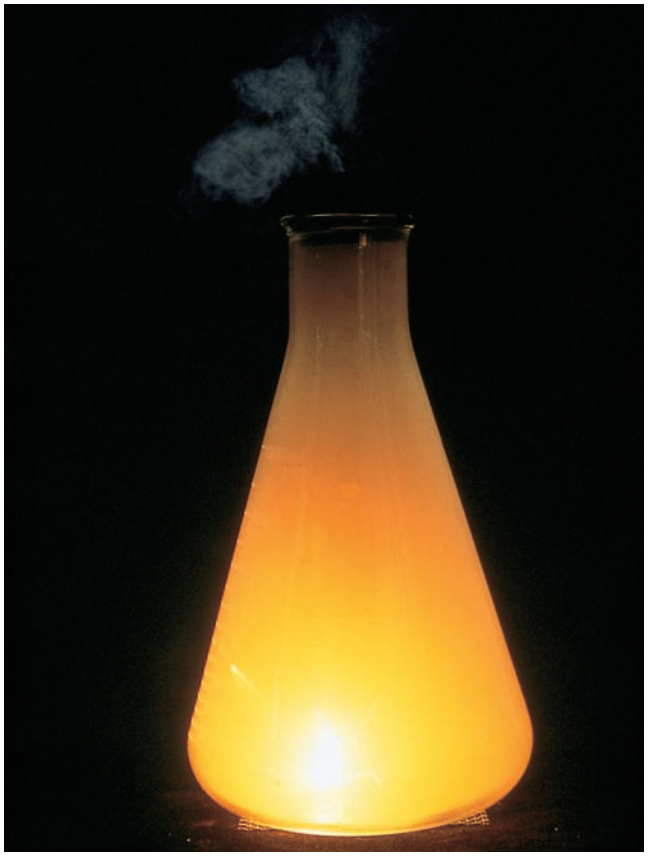
81. (a) Draw a Lewis diagram for carbonic acid, H_2CO_3, with a central carbon atom bonded to the three oxygen atoms.

(b) Carbonic acid is unstable in aqueous solution and converts to dissolved carbon dioxide. Use bond enthalpies to estimate the enthalpy change for the following reaction:

$$H_2CO_3 \longrightarrow H_2O + CO_2$$

CHAPTER 13

Spontaneous Processes and Thermodynamic Equilibrium



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The reaction between solid sodium and gaseous chlorine proceeds imperceptibly, if at all, until the addition of a drop of water sets it off.

In both fundamental research and practical applications of chemistry, chemical reactions are performed by mixing the reactants and regulating external conditions such as temperature and pressure. Two questions arise immediately:

1. Is it possible for the reaction to occur at the selected conditions?
2. If the reaction is possible, what determines the ratio of products and reactants at equilibrium?

Predicting the equilibrium composition for a chemical reaction is the central goal of Unit 4, and in this chapter, we develop the conceptual basis for answering these two key questions.

We can find out whether a proposed reaction is possible by determining whether it is a *spontaneous* thermodynamic process. In this context, "spontaneous" has a precise technical meaning (see later for clarification) that should not be confused with its conversational meaning, such as describing the spontaneous behavior of people in social situations. Thermodynamics can tell us whether a proposed reaction is possible under particular conditions even before we attempt the reaction. If the reaction is spontaneous, thermodynamics can also predict the ratio of products and reactants at equilibrium. But, we cannot use thermodynamics to predict the rate of a spontaneous reaction or how long it will take to reach equilibrium. These questions are the subject of chemical kinetics. To obtain a large amount of product from a spontaneous reaction in a short time, we need a reaction that is spontaneous *and* fast.

This chapter develops the thermodynamic methods for predicting whether a reaction is spontaneous, and Chapter 14 uses these results to determine the equilibrium ratio of products and reactants. Chapter 18 discusses the rates of chemical reactions. Manipulating conditions to optimize the yield of chemical reactions in practical applications requires the concepts from all three chapters.

The criteria for predicting spontaneity of physical and chemical processes are provided by the second law of thermodynamics, which is a brilliant abstraction and generalization from the observed facts of directionality in processes involving heat transfer. This is accomplished by introducing a new state function called *entropy*, which is denoted by S. The entropy function is defined so that the algebraic sign of its change, when we consider the total value in the system and the surroundings, is positive in the direction of a spontaneous process. Sections 13.1 through 13.5 develop the second law and demonstrate methods for calculating ΔS_{tot} and predicting spontaneity for simple physical processes in which chemical reactions are not involved.

When processes are conducted at constant T and P, the criteria for spontaneity and for equilibrium are stated more conveniently in terms of another state function called the *Gibbs free energy* (denoted by G), which is derived from S. Because chemical reactions are usually conducted at constant T and constant P, their thermodynamic description is based on ΔG rather than ΔS. This chapter concludes by restating the criteria for spontaneity of chemical reactions in terms of ΔG. Chapter 14 shows how to identify the equilibrium state of a reaction, and calculate the equilibrium constant from ΔG.

For all these reasons, ΔG is the most important thermodynamic concept in the entire field of chemical equilibrium. Your goals in this chapter should be to understand the meaning of the state function G, to become skilled in calculating its changes, ΔG, and to interpret both the magnitude and the algebraic sign of these changes.

13.1 The Nature of Spontaneous Processes

In preparation for setting up the second law of thermodynamics and stating precisely the criteria for spontaneity, we will examine several familiar examples of spontaneous processes and describe their features in general terms. A spontaneous change is one that *can* occur by itself without outside intervention, once conditions have been established for its initiation. The change may be fast or slow, and we may have to wait a significant period to determine whether it *does* occur.

One of the most striking features of spontaneous change is that it follows a specific direction when starting from a particular initial condition. A quite

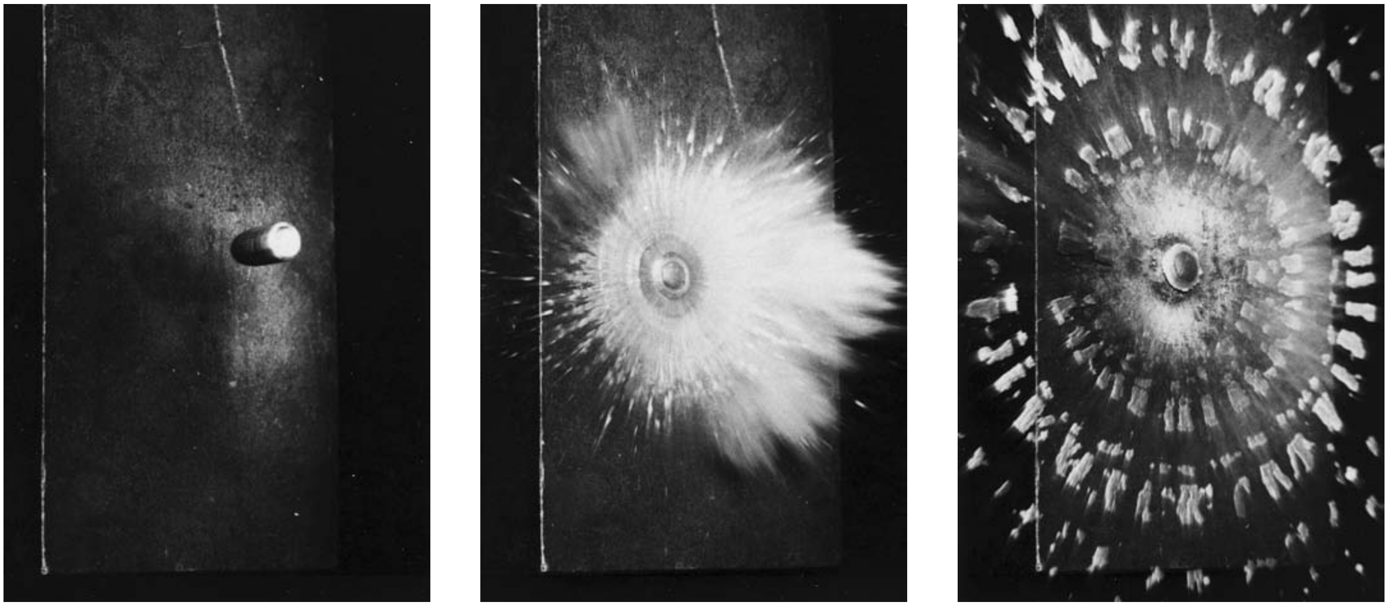


FIGURE 13.1 A bullet hitting a steel plate at a speed of 1600 ft/sec melts as its kinetic energy is converted to heat, and metal droplets spray in all directions. These three photographs make sense only in the order shown; the reverse process is unmistakably implausible.

(©Dr. Harold Edgerton/Palm Press, Inc.)

dramatic example is shown in the series of photographs in Figure 13.1, which show a speeding bullet that is fragmented on impact with a steel plate. We never observe a pile of metal fragments spontaneously assemble themselves into a speeding bullet. One of the goals of thermodynamics is to account for this *directionality* of spontaneous change. The first law of thermodynamics provides no guidance on this point. Energy is conserved both in a forward process and in its reverse; nothing in the first law indicates a preference for one direction of change over the other.

Spontaneous processes familiar in chemical laboratories also follow specific directions:

1. We measure *heat flowing* from a hot body to a cold one when they are brought into thermal contact, but we never detect heat flowing spontaneously in the opposite direction.
2. We observe a gas *expanding* into a region of lower pressure, but we never see the reverse process, a gas compressing itself spontaneously into a small part of its container.
3. We place a drop of red ink into a beaker of water and watch the color spread by *diffusion* of the ink particles until the water is uniformly pink, but we never see the ink spontaneously reorganize as a small red drop in a volume of otherwise colorless water.
4. We place 10 g sucrose (ordinary table sugar) in a beaker and add 100 mL water at 80°C. The sucrose *dissolves* to form a uniform solution. We never observe the spontaneous reappearance of a mound of sucrose at the bottom of a beaker of water.[1]
5. We open a container of acetone on the laboratory bench. We detect the aroma of acetone because some of the molecules have *evaporated* from the liquid and then diffused through the atmosphere to our position. We never observe the molecules to retreat spontaneously into the container.

---

[1] By intentional evaporation of the water, we can recover the sucrose. This constitutes a second process, which is beyond the spontaneous process of dissolution that is our immediate concern.

All the previous examples are physical processes that are both spontaneous and rapid. We initiate the process and see the result quickly thereafter, with no further intervention.

Like the simple physical processes described earlier, spontaneous chemical reactions are inherently directional. Ordinary experience shows that a mixture of hydrogen and oxygen gases exists indefinitely at room temperature. Yet, if the mixture is exposed to a small amount of powdered platinum metal, or an electric spark, the gases react explosively to produce water. The reverse reaction is not spontaneous; we never observe the spontaneous decomposition of water into gaseous hydrogen and oxygen. Figure 1.2 shows decomposition of water into hydrogen and oxygen gases by electrolysis in an electrochemical cell, where electrical energy is continually provided by the external circuit to drive this nonspontaneous reaction. Another example is shown in the photograph at the beginning of this chapter, where the reaction between sodium metal and chlorine gas occurs explosively after a drop of water is added. We never observe the spontaneous decomposition of sodium chloride into sodium metal and gaseous chlorine. A third example, less dramatic than the previous two, is the spontaneous reaction of copper metal with oxygen at room temperature. This is seen in many older municipal buildings, especially in Europe, where copper metal was used as roofing material. With time, these roofs develop the blue–green patina of copper oxides. We never observe the spontaneous reappearance of shiny metallic copper on these old roofs.

These three examples illustrate that the actual outcome of a spontaneous chemical reaction depends on the reaction rate. The possibility of reaction between hydrogen and oxygen was there all along, but the rate was too slow to be observed until the powdered metal or the electrical spark accelerated the reaction. The possibility of reaction between metallic copper and oxygen was there all along, and the rate was large enough to be observed, if not dramatically fast. Thermodynamics determines whether a reaction is possible, whereas chemical kinetics determines whether it is practical. At the end of this chapter, you will be able to predict whether a chemical reaction is spontaneous, and by the end of the next chapter, you will be able to predict its equilibrium state. But, you must wait until Chapter 18 to see whether a spontaneous reaction can be carried out at a useful rate.

The direction of each of these spontaneous processes is readily apparent by observing the initial and final states, regardless of their paths. This suggests the existence of a new *state function* that indicates the directionality of spontaneous processes. That state function will turn out to be **entropy,** and it will be defined so that the sign of its change indicates the direction in which a proposed process will be spontaneous. Entropy has the interesting property that we cannot predict spontaneity by considering the system alone; we must also consider the entropy changes in the surroundings during the process.

To develop the entropy function, we must first describe spontaneous processes in the language of thermodynamics summarized in Section 12.1. You should revisit each of the examples just discussed to see how it specifically fits this language. Initially, two objects in different thermodynamic states are brought into contact; one will be called "system" and the other "surroundings." Barriers (constraints) in place between them prevent their interaction. When the constraints are removed, a spontaneous process may occur in which the system and surroundings exchange energy and matter and in which the volume of both system and surroundings may change. Because the two together constitute a *thermodynamic universe,* the total amount of energy, volume, and matter shared between them is fixed. During the process, these quantities are redistributed between the system and surroundings.

Spontaneous processes are particular examples of irreversible processes defined in Section 12.1. In stark contrast with reversible processes, they do not proceed through a sequence of equilibrium states, and their direction cannot be reversed by an infinitesimal change in the direction of some externally applied force. Spontaneous processes cannot be represented as paths on the equation-of-state surface in Figure 12.1, but their initial and final equilibrium states can be represented as points on that surface.

What determines whether a process under consideration will be spontaneous? Where does a spontaneous process end? How are energy, volume, and matter partitioned between the system and surroundings at equilibrium? What is the nature of the final equilibrium state? These questions cannot be answered by the first law. Their answers require the second law and properties of the entropy, and a few developments are necessary before we can address these questions. We define entropy by molecular motions in Section 13.2 and by macroscopic process variables in Section 13.3. Finally, we present the methods for calculating entropy changes and for predicting spontaneity in Section 13.5.

13.2 Entropy and Spontaneity: A Molecular Statistical Interpretation

What is entropy and why should it be related to the spontaneity of processes in nature? These are deep questions that we can only begin to answer here. To do so, we step outside the confines of classical thermodynamics, which is concerned only with macroscopic properties, and examine the microscopic molecular basis for the second law. Such an approach, called **statistical thermodynamics,** shows that spontaneous change in nature can be understood by using probability theory to predict and explain the behavior of the many atoms and molecules that comprise a macroscopic sample of matter. Statistical thermodynamics also provides theoretical procedures for calculating the entropy of a system from molecular properties.

Spontaneity and Molecular Motions

Consider a particularly simple spontaneous process: the free *adiabatic* expansion of 1 mol of an ideal gas into a vacuum (Fig. 13.2). The gas is initially held in the left bulb in volume $V/2$, whereas the right bulb is evacuated. Before it is opened, the stopcock is a constraint that holds all the molecules in the left bulb. After the stopcock is opened, the gas expands to fill the entire volume, V.

Now examine the same free expansion from a microscopic point of view. Imagine that the path of one particular tagged molecule can be followed during the expansion and for some period of time after final equilibrium has been established, perhaps through a series of time-lapse snapshots showing the locations of all molecules in the gas. From its starting position on the left side at the beginning of the experiment, the tagged molecule will cross to the right, then back to the left, and so forth. If enough time elapses, the molecule will eventually spend equal amounts of time on the two sides, because there is no physical reason for it to prefer one side to the other. Recall from Section 9.5 that the molecules in an ideal gas do not collide with each other, and their kinetic energy does not change in collisions with the walls. The energy of the molecules remains the same at all locations, and the two sides of the container are identical. No experimental way exists to track the progress of one specific molecule in the gas; therefore, the best we can ask for is the *probability* that the molecule is on the left side at any given instant. (See Appendix C.6 for a review of probability concepts and methods.) The physical reasoning just summarized justifies that the probability that the molecule is on the left side will be $\frac{1}{2}$, the same as the probability that it is on the right side. Probability provides the key to understanding the direction of spontaneous change because it enables us to compare the likelihood of finding all the molecules on the left

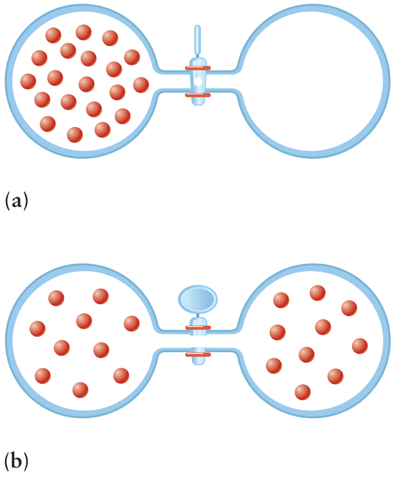


FIGURE 13.2 The free expansion of a gas into a vacuum. (a) The stopcock is closed with all gas in the left bulb. (b) With the stopcock open, half the gas is in each bulb.

side—after the constraint has been removed—with the likelihood of finding the molecules uniformly distributed over the combined volume of both sides.

Just how unlikely is a spontaneous compression of 1 mol gas from the combined volume back to the left side? The probability that one particular molecule is on the left side at a given time is $\frac{1}{2}$. A second specific molecule may be on either the left or the right, so the probability that both are on the left is $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$. As shown in Figure 13.3, in a gas containing a total of four molecules, all four molecules will be on the left only $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{16}$ of the time. Continuing this argument for all $N_A = 6.0 \times 10^{23}$ molecules leads to the probability that all N_A molecules are on the left:

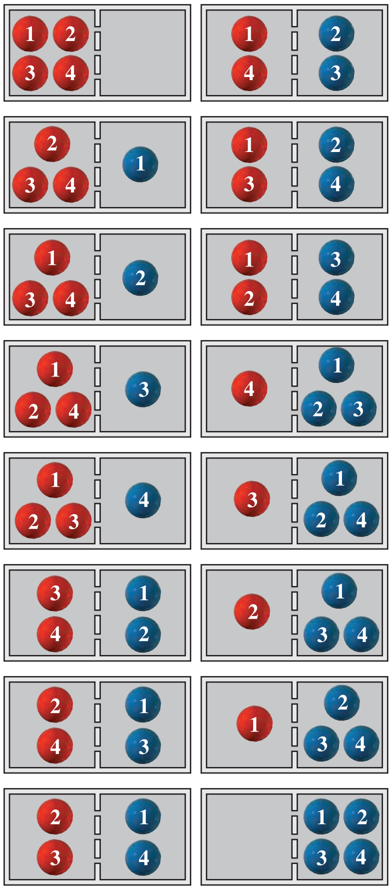


FIGURE 13.3 The 16 possible microstates of a system of 4 molecules that may occupy either side of a container. In only one of these are all four molecules on the left side.

$$\frac{1}{2} \times \frac{1}{2} \times \cdots \times \frac{1}{2} = \left(\frac{1}{2}\right)^{6.0 \times 10^{23}}$$

To evaluate this number, it is helpful to rewrite it in scientific notation as 1 divided by 10 raised to the power a (or, equivalently, as 10^{-a}):

$$\frac{1}{10^a} = \left(\frac{1}{2}\right)^{6.0 \times 10^{23}} = \frac{1}{2^{6.0 \times 10^{23}}}$$

A calculator can handle numbers this large (or this small) only if logarithms are used. Taking the base-10 logarithms of both denominators gives

$$\begin{aligned} a &= \log 2^{(6.0 \times 10^{23})} = 6.0 \times 10^{23} \log 2 \\ &= (6.0 \times 10^{23})(0.30) \\ &= 1.8 \times 10^{23} \end{aligned}$$

The probability that all the molecules will be on the left is 1 in $10^{1.8 \times 10^{23}}$.

This is a vanishingly small probability, because $10^{1.8 \times 10^{23}}$ is an unimaginably large number. It is vastly larger than the number 1.8×10^{23} (which is a large number already). To realize this, consider how such numbers would be written. The number 1.8×10^{23} is fairly straightforward to write out. It contains 22 zeros:

$$180{,}000{,}000{,}000{,}000{,}000{,}000{,}000$$

The number $10^{1.8 \times 10^{23}}$ is 1 followed by 1.8×10^{23} zeros. Written out, such a number would more than fill all the books in the world. Put in other terms, 1.8×10^{23} corresponds to the number of molecules in about 5 cm^3 water, but $10^{1.8 \times 10^{23}}$ is far larger than the number of molecules in the entire universe!

The statistical molecular picture explains that the gas expands to fill the whole available volume when the constraint is removed because this more uniform configuration of the molecules is overwhelmingly more probable than the initial configuration with all the molecules on the left side. The same explanation shows that the gas is never observed to compress spontaneously into a smaller volume because this nonuniform configuration of the molecules is overwhelmingly improbable in the absence of the constraint. Nothing in the laws of mechanics prevents a gas from compressing spontaneously. But this event is never seen because it is so improbable.

Thus, spontaneity in nature results from the random, statistical behavior of large numbers of molecules. *The directionality of spontaneous change is a consequence of the large numbers of molecules in the macroscopic systems treated by thermodynamics.* In systems containing fewer molecules, the situation can be quite different because the uniform configuration of molecules, although still the most probable, is no longer so overwhelmingly the most probable configuration. For example, if there were only 6 molecules, instead of 6×10^{23}, it would not be surprising to find them all on the left side at a given time. In fact, the probability that 6 molecules are on the left side is $\left(\frac{1}{2}\right)^6 = \frac{1}{64}$, so there is 1 chance in 64 that this will occur. Such small systems exhibit *statistical fluctuations* of the molecular configuration. Some of the fluctuations correspond to the initial nonuniform configuration maintained by the constraint, despite the absence of the constraint.

EXAMPLE 13.1

Calculate the probability of a spontaneous compression of 1.00 mol gas by 0.01%—that is, the probability that all the molecules will be found in a volume $V' = 0.9999V$ at a certain time.

SOLUTION

In this case, the probability that a given molecule is in V' is not $\frac{1}{2}$ but 0.9999 (the probability that it is in the remainder of V is 0.0001). The probability that all N_A molecules are in V' is

$$(0.9999)^{N_A} = 1/10^a$$

$$a = -N_A \log(0.9999) = (6.0 \times 10^{23})(4.3 \times 10^{-5})$$

$$= 2.6 \times 10^{19}$$

The chance of such a compression occurring spontaneously is 1 in $10^{2.6\times10^{19}}$, which is still vanishingly small. Thus, a spontaneous compression of even a fraction of a percent will not be seen.

Related Problems: 7, 8

Entropy and Molecular Motions

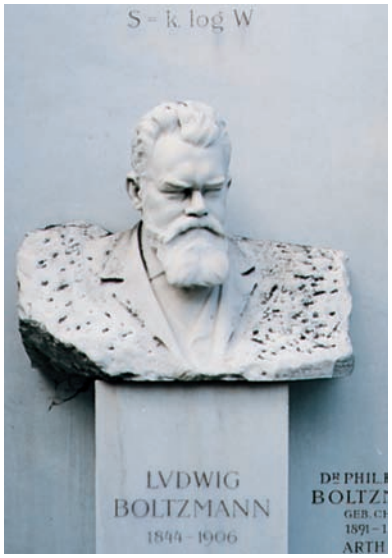
We want to define a new function called entropy that will increase when the system undergoes a spontaneous process. How can we relate entropy to the properties of the system and formulate a definition to achieve this goal? Spontaneous processes occur when constraints are removed from a system; the molecules respond by moving to explore the suddenly increased range of motions now available to them. In the free expansion of a gas, the molecules are initially confined in one part of the container. After the constraint is removed (the stopcock is opened), they are free to stay where they were, but they also are free to move throughout the larger combined volume of the two regions. Qualitatively, the numerical value of the entropy of a macroscopic system held in a particular thermodynamic state should depend on the *range of possible motions* (that is, the range of possible positions and momenta) available to the molecules while the system is held in that particular thermodynamic state. Any change in the macroscopic properties that enables the molecules to move out into larger regions of space or that increases the range of molecular speeds should increase the entropy of the system.

In preparation for defining entropy, we need a precise way to describe the "range of possible motions" of the molecules. This is accomplished by counting the number of microscopic, mechanical states, or **microstates,** available to molecules of the system. This number, denoted by Ω, counts all the possible combinations of positions and momenta available to the N molecules in the system when the system has internal energy U and volume V. For the simple model in Figure 13.3, $\Omega = 16$. In general, Ω is a function of U, V, and N, denoted as $\Omega(U, V, N)$. If the system is a monatomic ideal gas, the atoms do not interact. The position of each atom ranges freely throughout the entire volume, V. The internal energy consists of the total kinetic energy of the atoms, given as

$$U = \sum_{i=1}^{N} \varepsilon_i = \sum_{i=1}^{N} \frac{[p_{xi}^2 + p_{yi}^2 + p_{zi}^2]}{2m}$$

thus, the momenta of the atoms range through all values that satisfy the condition

$$2mU = \sum_{i=1}^{N} [p_{xi}^2 + p_{yi}^2 + p_{zi}^2]$$



Courtesy David Oxtoby

FIGURE 13.4 The fundamental relation between entropy (S) and the number of microstates (W) was derived by Ludwig Boltzmann in 1868. On his tombstone in Vienna is carved the equation he obtained, $S = k \log W$. We would write "ln" instead of "log" for the natural logarithm.

For a monatomic ideal gas, the value of Ω is given by

$$\Omega(U, V, N) = g\, V^N U^{(3N/2)}$$

where g is a collection of constants. Now imagine the walls defining the system are manipulated to change the values of U and V. The range of positions and momenta available to the molecules will increase or decrease accordingly. Because N is a very large number—of order 10^{23}—the value of Ω will increase or decrease dramatically when the volume of the system is increased or decreased in an expansion or compression, respectively. It will increase or decrease dramatically when the internal energy of the system is increased or decreased by heating or cooling, respectively.

The equation connecting entropy S and the number of available microstates Ω is

$$S = k_B \ln \Omega \qquad [13.1]$$

which was originally discovered by the Austrian physicist Ludwig Boltzmann in the late 19th century (Fig. 13.4). **Boltzmann's constant** k_B is identified as R/N_A, the ratio of the universal gas constant R to Avogadro's number N_A. Thus, entropy has the physical dimensions J K^{-1}. It is impossible to overstate the importance of Boltzmann's relation, because it provides the link between the microscopic world of atoms and molecules and the macroscopic world of bulk matter and thermodynamics. Although this equation holds quite generally, it is difficult to apply because calculating Ω is a daunting theoretical task except for the simplest ideal systems. Other equations are used for practical applications in statistical thermodynamics. For our purposes here, the equation provides qualitative insight into the physical meaning of entropy and qualitative interpretation of the magnitude and sign of entropy changes caused by specific thermodynamic processes. The following example illustrates these insights in a simple case in which only the volume of the system changes in the process.

EXAMPLE 13.2

Consider the free expansion of 1 mol gas from $V/2$ to V (see Fig. 13.2). Use Boltzmann's relation to estimate the change in entropy for this process.

SOLUTION

Consider the entire apparatus consisting of the filled and the evacuated bulbs to be a thermodynamic universe, so any exchange of thermal energy occurs solely between them; the pair of bulbs is taken to be thermally insulated from their surroundings. Then examine the effects of doubling V on Ω. If the volume is doubled, the number of positions available to a given molecule is doubled also. Therefore, the number of states available to the molecule should be proportional to the volume, V:

$$\text{number of states available per molecule} = cV$$

where c is a proportionality constant. The state of a *two*-molecule system is given jointly by the states of the molecules in it, so the number of microscopic states available is just the product of the number of states for each molecule, $(cV) \times (cV) = (cV)^2$. For an N-molecule system,

$$\text{microscopic states available} = \Omega = (cV)^N$$

Inserting this expression into Boltzmann's relation gives the entropy change for the free expansion of 1 mol (N_0 atoms) gas from a volume $V/2$ to V:

$$\Delta S(\text{microscopic}) = N_A k_B \ln(cV) - N_A k_B \ln(cV/2)$$

$$= N_A k_B \ln\left(\frac{cV}{cV/2}\right) = N_A k_B \ln 2$$

Note that the constant c has dropped out. The calculated change in entropy on expansion of the gas is clearly positive, which is consistent with the increase in the number of available microstates on expansion.

In the next section, the entropy change for this process from the macroscopic view will be calculated to be

$$\Delta S \text{ (thermodynamic)} = R \ln 2$$

illustrating explicitly that Boltzmann's microscopic description accurately explains the measured macroscopic results.

Related Problems: 3, 4, 5, 6, 7, 8, 9, 10

This example illustrates why Boltzmann's relation must involve the logarithmic function. Because entropy is an extensive variable, its value is proportional to N. But Ω depends on N through the *power* to which cV is raised. Therefore, doubling N doubles S but leads to Ω being squared. The only mathematical function that can connect two such quantities is the logarithm.

Examples of other processes in which the entropy of the system increases include phase transitions such as the melting of a solid. In a solid, the atoms or molecules are constrained to stay near their equilibrium positions in the crystal lattice, whereas in the liquid they can move far away from these fixed positions. More microstates are available to the molecules in the liquid, corresponding to an increase in entropy; for melting of a solid, ΔS_{sys} is positive. In the same way, the entropy increases for evaporation of a liquid because the number of microstates available to the molecules increases enormously. Whereas the molecules in a liquid remain at the bottom of their container, those in a gas move throughout the container, so the number of microstates increases upon vaporization. In some solid-solid phase transformations it is difficult to predict qualitatively which phase has higher entropy. Nonetheless, calculating the relative number of microstates available correctly predicts the sign of the entropy change in a transformation from one such phase to the other.

So far, we have considered microstates that involve only the positions of the molecules in a system. The distribution of energies can also contribute to the number of microstates. For example, a gas in which all the molecules have the same speed has fewer microstates available to it than does a gas with a distribution of molecular speeds; a spontaneous process is observed experimentally in which a system initially constrained to a single molecular speed moves toward the Maxwell–Boltzmann speed distribution, because this distribution maximizes the number of microstates available for a given total energy. Similarly, changes in bonding structures by forming molecules through chemical reactions can change the number of microstates. A mixture of hydrogen and oxygen molecules can increase its available microstates (and thus its entropy) if chemical bonds break and re-form to make water molecules. This reaction may be slow (or it may need a spark to set if off), but once it starts, the entropy will rise with the number of accessible microstates. This textbook gives only qualitative microscopic interpretations of these more complex examples. In later courses you will see more thorough interpretations based on the more advanced equations that replace Equation 13.1.

13.3 Entropy and Heat: Experimental Basis of the Second Law of Thermodynamics

This section defines the entropy function in terms of measurable macroscopic quantities to provide a basis for calculating changes in entropy for specific processes. The definition is part of the second law of thermodynamics, which is stated as an abstraction and generalization of engineering observations on the efficiency of heat engines. We start the discussion by presenting a nonmathematical qualitative summary of the arguments on efficiency. Then we define entropy and state the second law. Section 13.5 applies the definition to calculate entropy changes and to predict spontaneity of processes.

Section 13.4 presents a mathematical version of the same arguments set forth here. Either Section 13.3 or Section 13.4 provides adequate background for the calculations in Section 13.5, which are the heart of the second law.

Background of the Second Law of Thermodynamics

The second law of thermodynamics originated in practical concerns over the efficiency of steam engines at the dawn of the Industrial Age, late in the 18th century, and required about a century for its complete development as an engineering tool. The central issues in that development are summarized as follows. In each stroke of a steam engine, a quantity of hot steam at high pressure is injected into a piston-cylinder assembly, where it immediately expands and pushes the piston outward against an external load, doing useful work by moving the load. The external mechanical arrangement to which the piston is attached includes a reciprocating mechanism that returns the piston to its original position at the end of the stroke so that a new quantity of steam can be injected to start the next stroke. The engine operates as a cyclic process, returning to the same state at the beginning of each stroke. In each stroke, the expansion process is highly irreversible because the steam is cooled and exhausted from the cylinder at the end of the stroke. In essence, the engine extracts thermal energy from a hot reservoir, uses some of this energy to accomplish useful work, then discards the remainder into a cooler reservoir (the environment). The energy lost to the environment cannot be recovered by the engine. The internal combustion engine operates in a similar manner, with injection of hot steam replaced by in situ ignition of combustible fuel that burns in highly exothermic reactions. Its expansion process is similarly irreversible, and some of the energy expended by the hot gases is unrecoverable.

In both engines the efficiency (that is, the ratio of work accomplished *by* the engine in a cycle to the heat invested to drive that cycle) can be improved by reducing the unrecoverable losses to the environment in each cycle. Seeking to maximize efficiency, Sadi Carnot, an officer in Napoleon's French Army Corps of Engineers, modeled operation of the engine with an idealized cyclic process now known as the *Carnot cycle*. He concluded that unrecoverable losses of energy to the environment cannot be completely eliminated, no matter how carefully the engine is designed. Even if the engine is operated as a reversible process (in which case, displacement of the external load is too slow to be of practical interest), its efficiency cannot exceed a fundamental limit known as the *thermodynamic efficiency*. Thus, an engine with 100% efficiency cannot be constructed.

Carnot's conclusion has been restated in more general terms by the German physicist Rudolf Clausius in the following form:

> *There is no device that can transfer heat from a colder to a warmer reservoir without net expenditure of work.*

and by the English physicist Lord Kelvin in the following form:

> *There is no device that can transform heat withdrawn from a reservoir completely into work with no other effect.*

These statements are consistent with ordinary experience that (1) heat always flows spontaneously from a hotter body to a colder body, and that (2) work is always required to refrigerate a body. With confidence based on experience, Clausius, Kelvin, and later scientists and engineers have assumed these statements to be valid for *all* heat transfer processes and labeled them as equivalent formulations of the second law of thermodynamics.

Definition of Entropy

How do we apply these general statements to chemical processes such as the examples described in Section 13.1, which at first glance bear no resemblance to heat engines? Following the same reasoning that led Clausius and Kelvin to these statements, we define entropy and obtain an equation for the entropy change during a process. Highlights of the argument are summarized here, and a more detailed development is presented in the following section.

Carnot's analysis of efficiency for a heat engine operating *reversibly* showed that in each cycle q/T at the high temperature reservoir and q/T at the low temperature environment summed to zero:

$$\frac{q_{\mathrm{h}}}{T_{\mathrm{h}}} + \frac{q_l}{T_l} = 0$$

This result suggests that q/T is a state function because its value does not change in a cyclic process. Clausius extended this result to show that the quantity $\int(1/T)\,dq_{\mathrm{rev}}$ is independent of path in *any* reversible process and is, therefore, a state function. Clausius then *defined* the entropy change $\Delta S = S_{\mathrm{f}} - S_{\mathrm{i}}$ of a system in a process starting in state i and ending in state f by the equation

$$\Delta S = S_{\mathrm{f}} - S_{\mathrm{i}} = \int_{\mathrm{i}}^{\mathrm{f}} \frac{dq_{\mathrm{rev}}}{T} \qquad [13.2]$$

Entropy is therefore a state function and has physical dimensions J K^{-1}. We calculate $\Delta S = S_{\mathrm{f}} - S_{\mathrm{i}}$ for a specific process by (1) identifying its initial and final equilibrium states i and f as points on the equation-of-state surface in Figure 12.1, (2) selecting *any convenient reversible path* between them along which dq_{rev} and T are known, and (3) evaluating this integral along the selected path. It does not matter that the actual process of interest may be irreversible. Because entropy is a state function, its change depends only on the initial and final states, not at all on the path. Therefore, we are free to choose any reversible path that connects the initial and final states, purely on grounds of convenience, for calculating ΔS.

This is a beautiful consequence of the fact that S is a state function. Section 13.5 provides detailed procedures for calculating ΔS for numerous types of systems and processes. The calculated values of ΔS are then used to predict whether a particular contemplated process will be spontaneous.

The preceding discussion emphasizes that the second law, like all other laws of science, is a bold extrapolation of the results of a great deal of direct experimental observation under controlled conditions. The second law is not proved to be true by a single definitive experiment, it is not derived as a consequence of some more general theory, and it is not handed down by some higher authority. Rather, it is invoked as one of the "starting points" of thermodynamics, and conclusions drawn from its application to a great variety of irreversible processes (not necessarily involving heat engines) are compared with the results obtained in experimental studies. To date, no disagreements have been found between predictions properly made from the second law and the results of properly designed experiments.

A DEEPER LOOK

13.4 Carnot Cycles, Efficiency, and Entropy

This section provides a mathematical development of the relation between entropy and heat already presented qualitatively in Section 13.3. No additional results are obtained, but considerably greater insight is provided.

The Carnot Cycle

In a Carnot cycle (Fig. 13.5), a system traverses two isothermal and two adiabatic paths to return to its original state. Each path is carried out reversibly (that is, in thermal equilibrium, with internal and external forces nearly balanced at every step). As the system proceeds from state A to C through state B, the system performs work (Fig. 13.5a):

$$w_{\mathrm{ABC}} = -\int_{V_{\mathrm{A}}}^{V_{\mathrm{C}}} P\,dV$$

(Path ABC)

and it is clearly negative for this (expansion) process. If the system then returns from state C to A through state D,

$$w_{\mathrm{CDA}} = -\int_{V_{\mathrm{C}}}^{V_{\mathrm{A}}} P\,dV$$

(Path CDA)

which is now a positive quantity for this (compression) process; work is performed on the system (see Fig. 13.5b). In the course of the cycle, the work performed by the system is the area under curve ABC, whereas that performed on the system is the (smaller) area under curve ADC. The net result of the whole cycle is that work is performed by the system, and the amount of this work is the difference between the two areas, which is the area enclosed by the cycle (see Fig. 13.5c). As in any cyclic process, the overall energy change ΔU is zero, thus the net work equals the negative of the total heat added to the system.

We have not yet specified the material contained in the system. Assume initially that it is an ideal gas, for which the results from Section 12.6 apply directly, with T_{h} defined to be the higher temperature in the cycle and T_l the lower temperature.

Path AB: Isothermal Expansion (temperature T_{h})

$$w_{\mathrm{AB}} = -q_{\mathrm{AB}} = -nRT_{\mathrm{h}} \ln\left(\frac{V_{\mathrm{B}}}{V_{\mathrm{A}}}\right)$$

Path BC: Adiabatic Expansion

$$q_{\mathrm{BC}} = 0$$

$$w_{\mathrm{BC}} = nc_{\mathrm{V}}(T_l - T_{\mathrm{h}}) = -nc_{\mathrm{V}} - T_l)$$

Path CD: Isothermal Compression (temperature T_l)

$$w_{\mathrm{CD}} = -q_{\mathrm{CD}} = -nRT_l \ln\left(\frac{V_{\mathrm{D}}}{V_{\mathrm{C}}}\right)$$

$$= nRT_l \ln\left(\frac{V_{\mathrm{C}}}{V_{\mathrm{D}}}\right)$$

Path DA: Adiabatic Compression

$$q_{\mathrm{DA}} = 0$$

$$w_{\mathrm{DA}} = nc_{\mathrm{V}}(T_{\mathrm{h}} - T_{\mathrm{l}})$$

The net work done on the system is

$$\begin{aligned} w_{\mathrm{net}} &= w_{\mathrm{AB}} + w_{\mathrm{BC}} + w_{\mathrm{CD}} + w_{\mathrm{DA}} \\ &= -nRT_{\mathrm{h}} \ln\left(\frac{V_{\mathrm{B}}}{V_{\mathrm{A}}}\right) - nc_{\mathrm{V}}(T_{\mathrm{h}} - T_l) \\ &\quad + nRT_l \ln\left(\frac{V_{\mathrm{C}}}{V_{\mathrm{D}}}\right) + nc_{\mathrm{V}}(T_{\mathrm{h}} - T_l) \\ &= -nRT_{\mathrm{h}} \ln\left(\frac{V_{\mathrm{B}}}{V_{\mathrm{A}}}\right) + nRT_l \ln\left(\frac{V_{\mathrm{C}}}{V_{\mathrm{D}}}\right) \end{aligned}$$

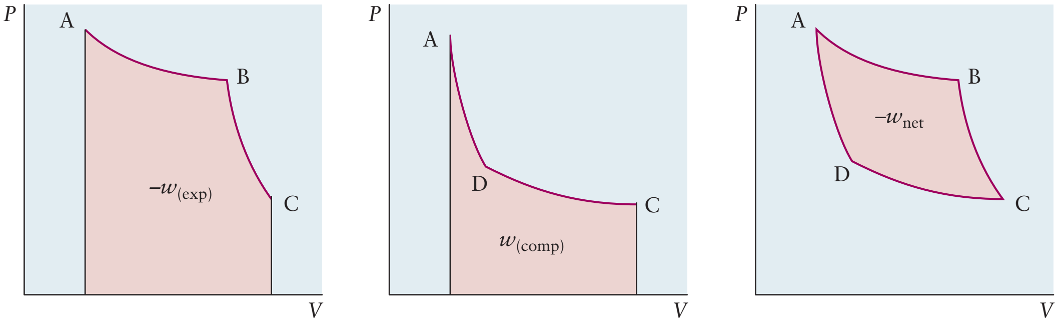
This can be simplified by noting that V_{B} and V_{C} lie on one adiabatic path, and V_{A} and V_{D} lie on another. In Section 12.6, the relation for a reversible adiabatic process was found:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

Hence,

$$\frac{T_{\mathrm{h}}}{T_l} = \left(\frac{V_{\mathrm{C}}}{V_{\mathrm{B}}}\right)^{\gamma - 1} \quad \text{for path BC}$$

FIGURE 13.5 Stages of the Carnot cycle. The work done by the system in expansion (a) and on the system by compression (b) is shown by the shaded areas. (c) The net work done per cycle is the area enclosed by the curve ABCDA.



(a) Expansion (b) Compression (c) Complete cycle and

$$\frac{T_h}{T_l} = \left(\frac{V_D}{V_A}\right)^{\gamma-1} \quad \text{for path DA}$$

Equating these expressions gives

$$\left(\frac{V_C}{V_D}\right)^{\gamma-1} = \left(\frac{V_D}{V_A}\right)^{\gamma-1}$$

or

$$\frac{V_C}{V_B} = \frac{V_D}{V_A} \text{ and } \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

Hence, the net work done in one passage around the Carnot cycle is

$$w_{net} = -nR(T_h - T_l) \ln \frac{V_B}{V_A} \qquad [13.3]$$

Heat Engines

The Carnot cycle is an idealized model for a heat engine. When a certain amount of heat, q_{AB}, is added to the system at the higher temperature, T_h, a net amount of work, $-w_{net}$, is obtained from the system. In addition, some heat q_{CD} is discharged at the lower temperature, but this energy is "degraded" and is no longer available for use in the engine. The **efficiency,** ϵ, of such an engine is the ratio of the negative of the net work done on the system, $-w_{net}$, to the heat added along the high-temperature isothermal path:

$$\epsilon = \frac{-w_{net}}{q_{AB}}$$

It is the net work that is available for the performance of useful mechanical tasks such as turning electrical generators or dynamos, but it is the heat, q_{AB}, absorbed at the higher temperature, T_h, that must be "paid for" in terms of coal or oil consumed to supply it. The efficiency, ϵ, must be maximized to get out the most work possible for the lowest cost.

For the ideal gas Carnot cycle, the efficiency is easily calculated:

$$\epsilon = \frac{-w_{net}}{q_{AB}} = \frac{nR(T_h - T_l)\ln(V_B/V_A)}{nRT_h \ln(V_B/V_A)}$$

$$\epsilon = \frac{T_h - T_l}{T_h} = 1 - \frac{T_l}{T_h} \qquad [13.4]$$

This result, called the Carnot efficiency or the **thermodynamic efficiency,** places a fundamental limit on the efficiency with which heat can be converted to mechanical work. Only if the high temperature, T_h, were infinite or the low temperature, T_l, were zero would it be possible to have a heat engine operate with 100% efficiency. To maximize efficiency, the greatest possible temperature difference should be used. Although we derived this result specifically for the ideal gas, we will show later in this section that it applies to *any* reversible engine operating between two temperatures. For a *real* engine, which must operate irreversibly, the actual efficiency must be lower than the thermodynamic efficiency.

EXAMPLE 13.3

Suppose a heat engine absorbs 10.0 kJ of heat from a high-temperature source at T_h = 450 K and discards heat to a low-temperature reservoir at T_l = 350 K. Calculate the thermodynamic efficiency, ϵ, of conversion of heat to work; the amount of work performed, $-w_{net}$; and the amount of heat discharged at T_l, q_{CD}.

SOLUTION

$$\epsilon = \frac{T_h - T_l}{T_h} = \frac{450 \text{ K} - 350 \text{ K}}{450 \text{ K}} = 0.222$$

Therefore, the engine can be, at most, 22.2% efficient. Because $\epsilon = -w_{net}/q_{AB}$,

$$w_{net} = -\epsilon q_{AB} = -(0.222)(10.0 \text{ kJ}) = -2.22 \text{ kJ}$$

Because ΔU for the whole cycle is 0,

$$\Delta U = 0 = q_{AB} + q_{CD} + w_{net}$$

$$q_{CD} = -q_{AB} - w_{net} = -10.0 + 2.22 = -7.8 \text{ kJ}$$

Therefore, 7.8 kJ is discharged at 350 K. This heat must be removed from the vicinity of the engine by a cooling system; otherwise, it will cause T_l to increase and reduce the efficiency of the engine.

Related Problems: 11, 12

Efficiency of General Carnot Engines

This subsection shows that all Carnot engines operating reversibly between two temperatures, T_h and T_l, have the same efficiency:

$$\varepsilon = \frac{-w_{net}}{q_h} = \frac{T_h - T_l}{T_h} \qquad [13.5]$$

That is, the efficiency calculated for an ideal gas applies equally to any other working fluid. To demonstrate this, we assume the *contrary* true and show that assumption leads to a contradiction with experience. The assumption is, therefore, deemed false.

Assume that there *are* two reversible machines operating between the same two temperatures, T_h and T_l, one of which has an efficiency, ϵ_1, that is greater than the efficiency, ϵ_2, of the other. The two machines are adjusted so that the total work output is the same for both. The more efficient machine is run as a heat engine so that it produces mechanical work $-w_1$. This work is used to operate the other machine in the opposite sense (as a heat pump) so that $w_2 = -w_1$. The net work input to the *combined* machines is then zero, because the work produced by the first machine is used to run the second.

Now, let's examine what happens to heat in this situation. Because engine 1 is more efficient than engine 2 and because the work is the same for both, engine 1 must withdraw less heat from the hot reservoir at T_h than is discharged into the same reservoir by engine 2; there is a net transfer of heat *into* the high-temperature reservoir. For the combined engines, $\Delta U_{tot} = w_{tot} = 0$; so q_{tot} must also be zero, and a net transfer of heat *out of* the low-temperature reservoir must therefore occur. By this reasoning we have devised an apparatus that can transfer heat from a low-temperature to a high-temperature reservoir with no net expenditure of work.

But that is impossible. All our experience shows we cannot make a device that transfers heat from a cold body to a hot body without doing work. In fact, exactly the opposite is seen: Heat flows spontaneously from hotter to colder bodies. Our experience is summarized and generalized in the following statement:

> *It is impossible to construct a device that will transfer heat from a cold reservoir to a hot reservoir in a continuous cycle with no net expenditure of work.*

This is one form of the second law of thermodynamics, as stated by Rudolf Clausius.

Further Discussion of Efficiency

Our assumption led to a conclusion that contradicts experience. Therefore, the original assumption must have been wrong, and there *cannot* be two reversible engines operating between the same two temperatures with different efficiencies. That is, all Carnot engines must have the same efficiency, which is

$$\epsilon = \frac{T_h - T_l}{T_h}$$

for the ideal gas. For any substance, ideal or not, undergoing a Carnot cycle,

$$\epsilon = \frac{-w_{net}}{q_h} = \frac{q_h + q_l}{q_h} = \frac{T_h - T_l}{T_h}$$

The Carnot cycle forms the basis for a *thermodynamic* scale of temperature. Because $\epsilon = 1 - (T_l/T_h)$, the Carnot efficiencies determine temperature ratios and thereby establish a temperature scale. The difficulty of operating real engines close to the reversible limit makes this procedure impractical. Instead, real gases at low pressures are used to define and determine temperatures (see Section 9.2).

The last two terms of the preceding equation can be rewritten as

$$1 + \frac{q_l}{q_h} = 1 - \frac{T_l}{T_h}$$

and simplified to

$$\boxed{\frac{q_h}{T_h} + \frac{q_l}{T_l} = 0} \qquad [13.6]$$

This simple equation has profound importance because it contains the essence of the second law of thermodynamics, namely, that q/T is a state function. To see this, consider a *general* reversible cyclic process and draw a series of closely spaced adiabats, as shown in Figure 13.6. (An adiabat is a curve on the PV diagram showing those thermodynamic states connected by a particular reversible adiabatic process.) Now replace each segment along the given cycle (ABCDA) with a series of alternating isothermal and adiabatic segments. Clearly, we can construct a path that is arbitrarily close to the desired curve by taking more and more closely spaced adiabats.

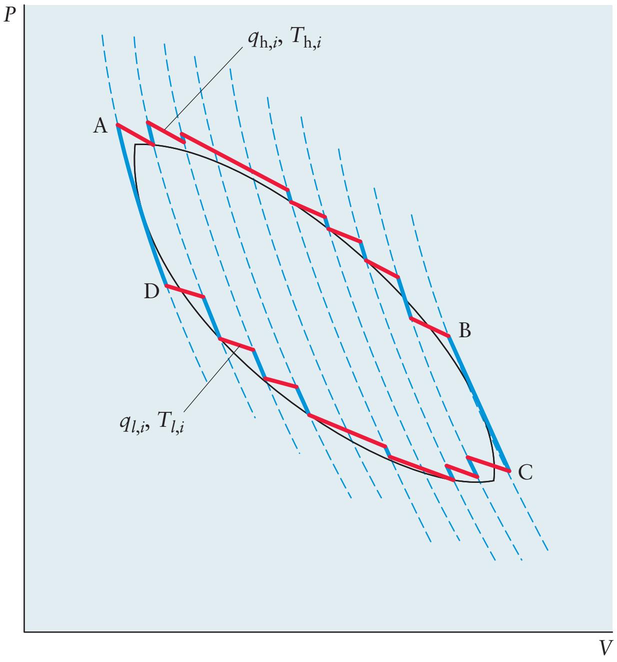


FIGURE 13.6 A general cyclic process (ABCDA) can be approximated to arbitrary accuracy by the sum of a series of Carnot cycles.

Now follow the evolution of $\Sigma_i(q_i/T_i)$ along this curve. The key observation is that the contributions q_i/T_i appear in pairs: For each $q_{h,i}/T_{h,i}$ from an isothermal segment along the ABC path, there is a $q_{l,i}/T_{l,i}$ along the CDA path. Any given pair forms two sides of a Carnot cycle, with the other two sides determined by adiabats; thus,

$$\frac{q_{h,i}}{T_{h,i}} + \frac{q_{l,i}}{T_{l,i}} = 0$$

Summing over i shows that

$$\sum_i \left(\frac{q_{h,i}}{T_{h,i}} + \frac{q_{l,i}}{T_{l,i}}\right) = 0$$

Because this summation follows the original reversible path to an arbitrary accuracy (if the lengths of the segments are made short enough), it follows that

$$\oint \frac{1}{T}\, dq_{rev} = 0$$

for *any* closed, reversible path. Although q is not a state function, q_{rev}/T is a state function because, like energy and enthalpy, its total change is zero for any process that begins and ends in the same state. From this result, Clausius *defined* the entropy change $\Delta S = S_f - S_i$ of a system in a process starting in state i and ending in state f by the equation

$$\boxed{\Delta S = \int_i^f \frac{dq_{rev}}{T}} \qquad [13.7]$$

As we have stated, the principles of thermodynamics are based on observations of nature and are not subject to mathematical proof. We have accomplished something quite significant, however. From the assumption—based on physical observation—that heat cannot be transferred from a low-temperature to a high-temperature body without expenditure of work, we have derived the result that $\int(1/T)\,dq_{\text{rev}}$ is independent of path and, therefore, is a state function. This result has been subjected to rigorous testing and no proper test has found it to be invalid. Therefore, we have great confidence in the generality of this result and are entirely comfortable in calling it a scientific law. Some critics might say, "If we have to make some assumption anyway, why don't we just assume that $\int(1/T)\,dq_{\text{rev}}$ is path independent to start with?" This is certainly possible and is practiced in many presentations of thermodynamics. Our approach is different; we prefer to base our assumptions directly on physical observation, not on abstract mathematical axioms.

13.5 Entropy Changes and Spontaneity

This section outlines procedures for calculating entropy changes that occur in the system and in the surroundings during several types of processes. The final subsections show how entropy changes calculated for the thermodynamic universe (system plus surroundings) predict whether a particular contemplated process can occur spontaneously when attempted in the laboratory or in a chemical plant.

ΔS_{sys} for Isothermal Processes

If the reversible process selected as the pathway connecting the initial and final states is isothermal, the calculation simplifies immediately. Because T is constant, it comes outside the integral:

$$\Delta S = \int_{\text{i}}^{\text{f}} \frac{dq_{\text{rev}}}{T} = \frac{1}{T}\int_{\text{i}}^{\text{f}} dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} \qquad [13.8]$$

Here, q_{rev} is the *finite* amount of heat absorbed by the system during the entire reversible isothermal process.

COMPRESSION/EXPANSION OF AN IDEAL GAS Consider an ideal gas enclosed in a piston-cylinder arrangement that is maintained at constant temperature in a heat bath. The gas can be compressed (or expanded) reversibly by changing the position of the piston to accomplish a specified change in volume. In Section 12.6, the heat transferred between system and bath when the gas is expanded (or compressed) isothermally and reversibly from volume V_1 to V_2 is shown to be

$$q_{\text{rev}} = nRT \ln\left(\frac{V_2}{V_1}\right)$$

The resulting change in entropy, therefore, is

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right) \quad \text{(constant } T) \qquad [13.9]$$

From Equation 13.9 we see that the entropy of a gas increases during an isothermal expansion ($V_2 > V_1$) and decreases during a compression ($V_2 < V_1$). Boltzmann's relation (see Eq. 13.1) provides the molecular interpretation of these results. The number of microstates available to the system, Ω, increases as the volume of the system increases and decreases as volume decreases, and the entropy of the system increases or decreases accordingly.

PHASE TRANSITIONS Another type of constant-temperature process is a phase transition such as the melting of a solid at constant pressure. This occurs reversibly at the fusion temperature, T_f, because an infinitesimal change in external conditions, such as reducing the temperature, can reverse the melting process. The reversible heat when 1 mol of substance melts is $q_{rev} = \Delta H_{fus}$, so

$$\Delta S_{fus} = \frac{q_{rev}}{T_f} = \frac{\Delta H_{fus}}{T_f} \qquad [13.10]$$

The entropy increases when a solid melts or a liquid vaporizes, and it decreases when the phase transition occurs in the opposite direction. Again, Boltzmann's relation provides the molecular interpretation. When a solid melts or a liquid vaporizes, the number of accessible microstates Ω increases, and thus the entropy increases.

EXAMPLE 13.4

Calculate the entropy change when 3.00 mol benzene vaporizes reversibly at its normal boiling point of 80.1°C. The molar enthalpy of vaporization of benzene at this temperature is 30.8 kJ mol^{-1}.

SOLUTION

The entropy change when 1 mol benzene is vaporized at 80.1°C (=353.25 K) is

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} = \frac{30{,}800 \text{ J mol}^{-1}}{353.25 \text{ K}} = +87.2 \text{ J K}^{-1}$$

When 3.00 mol is vaporized, the entropy change is three times as great:

$$\Delta S = (3.00 \text{ mol})(+87.2 \text{ J K}^{-1} \text{ mol}^{-1}) = +262 \text{ J K}^{-1}$$

Related Problems: 13, 14

Remarkably, most liquids have similar values for the molar entropy of vaporization. **Trouton's rule** summarizes this observation:

$$\Delta S_{vap} = 88 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1} \qquad [13.11]$$

Note that the ΔS_{vap} of benzene, calculated in Example 13.4, is within this range. The constancy of ΔS_{vap} means that ΔH_{vap} and T_b, which vary widely from substance to substance, must do so in the same proportion. Trouton's rule allows enthalpies of vaporization to be estimated from boiling temperatures. However, exceptions exist; the molar entropy of vaporization for water is 109 J K^{-1} mol^{-1}. The value for water is unusually high because hydrogen bonding in liquid water means there are many fewer allowed configurations (lower entropy) than in other liquids; thus, water shows a much greater increase in the number of microstates on vaporization.

ΔS_{sys} for Processes with Changing Temperature

Now consider a reversible process in which the temperature changes. In this case, Equation 13.2 must be used:

$$\Delta S = \int_A^B \frac{1}{T}\, dq_{rev}$$

In the integral, A and B represent, respectively, the initial and final equilibrium states for the process. The calculation must be conducted along a reversible path connecting A and B. For a reversible *adiabatic* process, $q = 0$ and, therefore, $\Delta S = 0$. Such a process is also called **isentropic** (that is, the entropy is constant).

In a reversible *isochoric* process, the volume is held constant and the system is heated or cooled by contact with a reservoir whose temperature differs from that of the system by an infinitesimal amount, dT. The heat transferred in this case is

$$dq_{\text{rev}} = nc_{\text{V}}\, dT$$

and the entropy change of the system as it is heated from T_1 to T_2 is

$$\Delta S = \int_{T_1}^{T_2} \frac{1}{T}\, dq_{\text{rev}} = \int_{T_1}^{T_2} \frac{nc_{\text{V}}}{T}\, dT$$

If c_{V} is independent of T over the temperature range of interest, it can be removed from the integral, giving the result

$$\Delta S = nc_{\text{V}} \int_{T_1}^{T_2} \frac{1}{T}\, dT = nc_{\text{V}} \ln\left(\frac{T_2}{T_1}\right) \quad \text{(constant } V\text{)} \qquad [13.12]$$

The analogous result for the entropy change of the system in a reversible *isobaric* process (constant *pressure*) is

$$\Delta S = \int_{T_1}^{T_2} \frac{nc_{\text{P}}}{T}\, dT = nc_{\text{P}} \ln\left(\frac{T_2}{T_1}\right) \quad \text{(constant } P\text{)} \qquad [13.13]$$

Entropy always increases with increasing temperature. From the kinetic theory of ideal gases in Chapter 9, it is clear that increasing the temperature of the gas increases the magnitude of the average kinetic energy per molecule and, therefore, the range of momenta available to molecules. This, in turn, increases Ω for the gas and, by Boltzmann's relation, the entropy of the gas.

Now consider an experiment in which identical samples of a gas are taken through identical temperature increases, one sample at constant V and the other at constant P. Let's compare the entropy changes in the two processes. From the previous discussion it follows that $\Delta S_{\text{P}} > \Delta S_{\text{V}}$ because $c_{\text{P}} > c_{\text{V}}$. The molecular interpretation is based on the discussion of c_{P} and c_{V} in Section 12.3. The gas heated at constant P increases in volume, as well as in temperature; its molecules therefore gain access to a greater range of positions, as well as a greater range of momenta. Consequently, the gas heated at constant P experiences a *greater* increase in Ω than does the gas heated at constant V and, therefore, a greater increase in S.

The following example illustrates that the entropy is a state function, for which changes are independent of the path followed.

EXAMPLE 13.5

(a) Calculate the entropy change for the process described in Example 12.9: 5.00 mol argon expands reversibly at a constant temperature of 298 K from a pressure of 10.0 to 1.00 atm.

(b) Calculate the entropy change for the same initial and final states as in part **(a)** but along a different path. First, the 5.00 mol argon expands reversibly and *adiabatically* between the same two pressures. This is the path followed in Example 12.10; it causes the temperature to decrease to 118.6 K. Then the gas is heated at constant pressure back to 298 K.

SOLUTION

(a) At constant temperature, the entropy change is

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right) = nR \ln\left(\frac{P_1}{P_2}\right)$$

$$= (5.00 \text{ mol})(8.315 \text{ J K}^{-1} \text{ mol}^{-1}) \ln 10.0$$

$$= +95.7 \text{ J K}^{-1}$$

(b) For the adiabatic part of this path, the entropy change is zero. When the gas is then heated reversibly at constant pressure from 118.6 to 298 K, the entropy change is

$$\Delta S = nc_{\text{P}} \ln\left(\frac{T_2}{T_1}\right)$$

$$= (5.00 \text{ mol})\left(\frac{5}{2} \times 8.315 \text{ J K}^{-1} \text{ mol}^{-1}\right) \ln \frac{298 \text{ K}}{118.6\ K}$$

$$= +95.7 \text{ J K}^{-1}$$

This is the same as the result from part (**a**), an illustration of the fact that the entropy is a state function. By contrast, the amounts of heat for the two paths are different: 28.5 and 18.6 kJ.

Related Problems: 17, 18

ΔS for Surroundings

Usually, the surroundings can be treated as a large *heat bath* that transfers heat to or from the system at the fixed temperature of the bath. In such cases, the heat capacity of the surroundings (heat bath) must be so large that the heat transferred during the process does not change the temperature of the bath. The heat gained by the surroundings during a process is the heat lost from the system. If the process occurs at constant P, then

$$q_{\text{surr}} = -\Delta H_{\text{sys}}$$

and the entropy change of the surroundings is

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T_{\text{surr}}} \qquad [13.14]$$

If the process occurring in the system is exothermic, the surroundings gain heat and the entropy change of the surroundings is positive. Similarly, an endothermic process in the system is accompanied by a negative entropy change in the surroundings, because the surroundings give up heat during the process to keep the system at the temperature of the heat bath.

If the surroundings lack sufficient heat capacity to maintain constant temperature during the process, then entropy changes for the surroundings must be calculated by the methods just demonstrated for the system, taking explicit account of the temperature change of the surroundings. Examples of both cases are included in the problems at the end of this chapter.

ΔS_{tot} for System Plus Surroundings

The tools are now in place for using the second law to predict whether specific processes will be spontaneous. We illustrate the procedure first for spontaneous cooling of a hot body, and then for irreversible expansion of an ideal gas.

SPONTANEOUS COOLING OF A HOT BODY Consider a spontaneous process in which a sample of hot metal is cooled by sudden immersion in a cold bath. Heat flows from the metal into the bath until they arrive at the same temperature. This spontaneous process is accompanied by an increase in the total entropy for the thermodynamic universe of the process, as illustrated by the following example.

EXAMPLE 13.6

A well-insulated ice-water bath at 0.0°C contains 20 g ice. Throughout this experiment, the bath is maintained at the constant pressure of 1 atm. When a piece of nickel at 100°C is dropped into the bath, 10.0 g of the ice melts. Calculate the total entropy change for the thermodynamic universe of this process. (Specific heats at constant *P:* nickel, 0.46 $\text{J K}^{-1}\ \text{g}^{-1}$; water, 4.18 $\text{J K}^{-1}\ \text{g}^{-1}$; ice, 2.09 $\text{J K}^{-1}\ \text{g}^{-1}$. Enthalpy of fusion of ice, 334 $\text{J K}^{-1}\ \text{g}^{-1}$.)

SOLUTION

Consider the nickel to be the *system* and the ice-water bath to be the *surroundings* in this experiment. Heat flows from the nickel into the bath and melts some of the ice. Consequently, the entropy of the nickel decreases and the entropy of the bath increases. The final equilibrium temperature of both system and bath is 0.0°C, as indicated by the presence of some ice in the bath at equilibrium.

Before calculating ΔS_{Ni} it is necessary to calculate the mass of the nickel from the calorimetry equation as follows:

$$\text{heat lost by Ni} = \text{heat gained by ice bath} = \text{heat used in melting ice}$$

$$-M\,(0.46\ \text{J K}^{-1}\ \text{g}^{-1})(273.15\ \text{K} - 373.15\ \text{K}) = (10.0\ \text{g})(334\ \text{J g}^{-1})$$

$$M = 73\ \text{g}$$

Because the nickel is cooled at constant *P,* the entropy change for the nickel is calculated as

$$\Delta S_{\text{Ni}} = (73\ \text{g})(0.46\ \text{J g}^{-1}\ \text{K}^{-1}) \ln (0.73) = -10\ \text{J K}^{-1}$$

Because the ice bath has remained at constant T throughout the experiment, it can be treated as a "large heat bath," and its entropy change is calculated as

$$\Delta S_{\text{bath}} = \frac{-\Delta H_{\text{sys}}}{T_{\text{bath}}} = \frac{-(-334\ \text{J g}^{-1})(10.0\ \text{g})}{273.15\ \text{K}} = 12\ \text{J K}^{-1}$$

Now,

$$\Delta S_{\text{tot}} = \Delta S_{\text{Ni}} + \Delta S_{\text{bath}} = -10 + 12 = +2\ \text{J K}^{-1}$$

Thus, the process is spontaneous, driven by the fact that the entropy gain of the melting ice exceeds the entropy loss of the cooling metal.

Related Problems: 20, 21, 22

IRREVERSIBLE EXPANSION OF AN IDEAL GAS Consider a gas confined within a piston-cylinder arrangement and held at constant temperature in a heat bath. Suppose the external pressure is abruptly reduced and held constant at the new lower value. The gas immediately expands against the piston until its internal pressure declines to match the new external pressure. The total entropy of system plus surroundings will increase during this expansion. In preparation for a quantitative example, a general comparison of irreversible and reversible processes connecting the same initial and final states provides insight into why the total entropy increases in a spontaneous process.

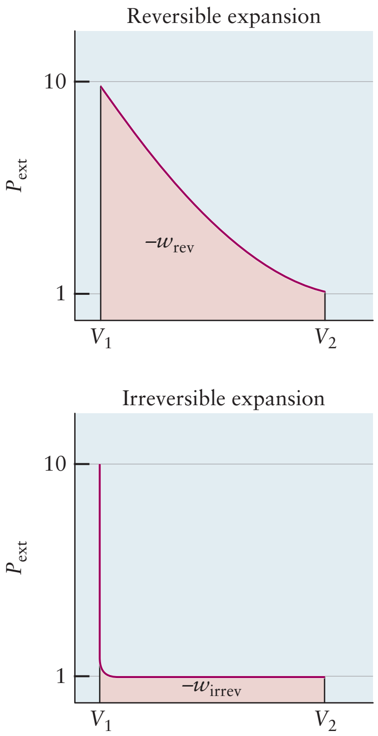


FIGURE 13.7 Work done by a system in reversible and irreversible expansions between the same initial and final states. The work performed is greater for the reversible process.

The work performed *by* a system ($-w$) as it undergoes an irreversible isothermal expansion is always less than when the expansion is conducted reversibly. To see this, return to the definition of work done *on* a system:

$$w = -\int P_{ext}\,dV$$

During an expansion, P_{ext} must be less than P, the pressure of the gas. For a reversible expansion, P_{ext} is only infinitesimally smaller (so the system is always close to equilibrium); but for an irreversible expansion, P_{ext} is measurably smaller. Therefore, the area under a graph of P_{ext} plotted against V is less than that of a graph of P against V (Fig. 13.7), so

$$-w_{irrev} = \int P_{ext}\,dV < \int P\,dV = -w_{rev}$$

and the work performed by the system, $-w_{irrev}$, is algebraically less than $-w_{rev}$. If the system is viewed as an "engine" for performing useful work on the surroundings, a reversible process is always more efficient than an irreversible one.

If the reversible and irreversible processes have the same initial and final states, then ΔU is the same for both.

$$\Delta U = w_{irrev} + q_{irrev} = w_{rev} + q_{rev}$$

But because

$$-w_{irrev} < -w_{rev}$$

we must have

$$w_{irrev} > w_{rev}$$

and

$$q_{irrev} < q_{rev}$$

The heat absorbed is a *maximum* when the process is conducted reversibly.

The following example illustrates these inequalities.

EXAMPLE 13.7

Calculate the heat absorbed and the work done on a system of 5.00 mol of an ideal gas as it expands irreversibly at constant temperature $T = 298$ K from a pressure of 10.0 to 1.00 atm. The external pressure is held constant at 1.00 atm.

SOLUTION

The initial volume V_1 is

$$V_1 = \frac{nRT}{P_1} = \frac{(5.00\text{ mol})(0.08206\text{ L atm K}^{-1}\text{ mol}^{-1})(298\text{ K})}{10.0\text{ atm}} = 12.2\text{ L}$$

The final volume is 10 times this, or

$$V_2 = 122\text{ L}$$

For a constant external pressure,

$$\begin{aligned} w_{irrev} &= -P_{ext}\Delta V = -(1.00\text{ atm})(122\text{ L} - 12.2L) = -110\text{ L atm} \\ &= -11.1\text{ kJ} \end{aligned}$$

At constant T, $\Delta U = 0$, however, so

$$q_{irrev} = -w_{irrev} = 11.1\text{ kJ}$$

In Example 12.9, a reversible expansion between the same two states was carried out, with the result that

$$w_{\text{rev}} = -28.5 \text{ kJ}$$

This demonstrates that

$$-w_{\text{irrev}} < -w_{\text{rev}}$$

and

$$q_{\text{irrev}} < q_{\text{rev}}$$

For reversible and irreversible processes connecting the same pair of initial and final states, it is always true that

$$q_{\text{rev}} > q_{\text{irrev}}$$

Dividing this expression by T, the temperature at which the heat is transferred, gives

$$\frac{q_{\text{rev}}}{T} > \frac{q_{\text{irrev}}}{T}$$

The left side is the entropy change ΔS,

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

so

$$\Delta S > \frac{q_{\text{irrev}}}{T}$$

The last two equations can be combined as

$$\Delta S \geq \frac{q}{T}$$

where the equality applies only to a reversible process. This expression, called the **inequality of Clausius,** states that in any spontaneous process the heat absorbed by the system from surroundings at the same temperature is always less than $T\Delta S$. In a reversible process, the heat absorbed is equal to $T\Delta S$.

Now let's apply Clausius's inequality to processes occurring within an *isolated* system. In this case, there is no transfer of heat into or out of the system, and $q = 0$. Therefore, for spontaneous processes within an isolated system, $\Delta S > 0$.

The thermodynamic universe of a process (that is, a system plus its surroundings) is clearly an isolated system to which Clausius's inequality can be applied. It follows that

1. *In a* reversible *process the total entropy of a system plus its surroundings is unchanged.*
2. *In an* irreversible *process the total entropy of a system plus its surroundings must increase.*
3. *A process for which* $\Delta S_{\text{total}} < 0$ *is impossible.*

These statements constitute the heart of the second law, because they provide its predictive power.

EXAMPLE 13.8

Calculate $\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ for the reversible and irreversible isothermal expansions of Examples 12.9 and 13.7.

SOLUTION

For the reversible expansion,

$$q_{\text{rev}} = 28.5 \text{ kJ}$$

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T} = \frac{28{,}500 \text{ J}}{298 \text{ K}} = +95.7 \text{ J K}^{-1}$$

The surroundings give up the same amount of heat at the same temperature. Hence,

$$\Delta S_{\text{surr}} = \frac{-28{,}500 \text{ J}}{298 \text{ K}} = -95.7 \text{ J K}^{-1}$$

or $\Delta S_{\text{tot}} = 95.7 - 95.7 = 0$ for the reversible process. For the irreversible expansion, it is still true that

$$\Delta S_{\text{sys}} = +95.7 \text{ J K}^{-1}$$

because S is a function of state, and the initial and final states are the same as for the reversible expansion. From Example 13.7, only 11.1 kJ of heat is given up by the surroundings in this case.[2] Hence,

$$\Delta S_{\text{surr}} = \frac{-11{,}100 \text{ J}}{298 \text{ K}} = -37.2 \text{ J K}^{-1}$$

and $\Delta S_{\text{tot}} = 95.7 - 37.2 = 58.5 \text{ J K}^{-1} > 0$ for the irreversible process.

13.6 The Third Law of Thermodynamics

In thermodynamic processes, only *changes* in entropy, ΔS, are measured, just as only changes in internal energy, ΔU, or enthalpy, ΔH, are measured. It is nevertheless useful to define absolute values of entropy relative to some reference state. An important experimental observation that simplifies the choice of reference state is:

> *In any thermodynamic process involving only pure phases in their equilibrium states, the entropy change ΔS approaches zero as T approaches 0 K.*

This observation is the **Nernst heat theorem,** named after its discoverer, the German physicist Walther Nernst. It immediately suggests a choice of reference state: The entropy of any pure element in its equilibrium state is defined to approach zero as T approaches 0 K. From the Nernst theorem, the entropy change for any chemical reaction, including one in which elements react to give a pure compound, approaches zero at 0 K. The most general form of this statement is the **third law of thermodynamics:**

> *The entropy of any pure substance (element or compound) in its equilibrium state approaches zero at the absolute zero of temperature.*

Absolute zero can never actually be reached; therefore, a small extrapolation is needed to make use of this result.

---

[2] How can the heat from Example 13.7, which is irreversible from the perspective of the system, be reversible from the perspective of the surroundings? This can be accomplished by enclosing the gas in a material (such as a metal) that can efficiently transfer heat to and from the surroundings, and thus remain close to equilibrium, at the same time that the gas itself is far from equilibrium due to the gas currents that occur during the irreversible expansion.

The third law, like the two laws that precede it, is a macroscopic law based on experimental measurements. It is consistent with the microscopic interpretation of the entropy presented in Section 13.2. From quantum mechanics and statistical thermodynamics, we know that the number of microstates available to a substance at equilibrium falls rapidly toward one as the temperature approaches absolute zero. Therefore, the absolute entropy defined as $k_B \ln \Omega$ should approach zero. The third law states that the entropy of a substance in its equilibrium state approaches zero at 0 K. In practice, equilibrium may be difficult to achieve at low temperatures, because particle motion becomes very slow. In solid CO, molecules remain randomly oriented (CO or OC) as the crystal is cooled, even though in the equilibrium state at low temperatures, each molecule would have a definite orientation. Because a molecule reorients slowly at low temperatures, such a crystal may not reach its equilibrium state in a measurable period. A nonzero entropy measured at low temperatures indicates that the system is not in equilibrium.

Standard-State Entropies

Because the entropy of any substance in its equilibrium state is zero at absolute zero, its entropy at any other temperature T is given by the entropy increase as it is heated from 0 K to T. If heat is added at constant pressure,

$$\Delta S = n \int_{T_1}^{T_2} \frac{c_P}{T}\, dT$$

Thus, S_T, the absolute entropy of 1 mol of substance at temperature T, is given by

$$S_T = \int_0^T \frac{c_P}{T}\, dT$$

It is necessary merely to measure c_P as a function of temperature and determine the area under a plot of c_P/T versus T from 0 K to any desired temperature. If a substance melts, boils, or undergoes some other phase change before reaching the temperature T, the entropy change for that process must be added to $\int (c_P/T)\, dT$.

To calculate entropy changes for chemical reactions, we find it convenient to use the same standard state already selected for enthalpy calculations in Section 12.3. For this purpose, we define the **standard molar entropy** to be the absolute molar entropy $S°$ at 298.15 K and 1 atm pressure (Fig. 13.8):

$$S° = \int_0^{298.15} \frac{c_P}{T}\, dT + \Delta S \text{ (phase changes between 0 and 298.15 K)} \qquad [13.15]$$

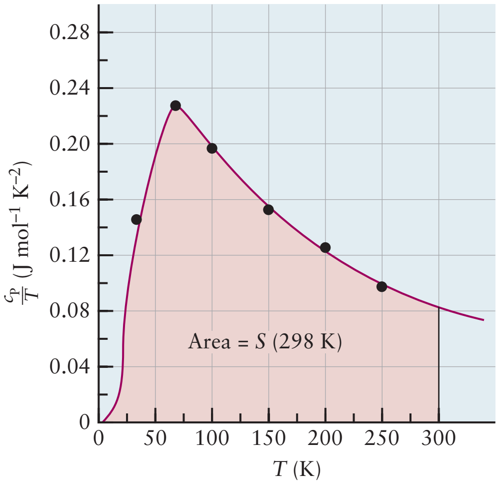


FIGURE 13.8 A graph of c_P/T versus T for platinum. The black dots represent experimental measurements. The area up to any temperature (here, 298 K) is the molar entropy at that temperature.

Standard molar entropies $S°$ are tabulated for a number of elements and compounds in Appendix D. If c_P is measured in J K^{-1} mol^{-1}, then the entropy $S°$ will have the same units. For dissolved ions, the arbitrary convention $S°\ (H^+(aq)) = 0$ is applied (just as for the standard enthalpy of formation of H^+ discussed in Section 12.3). For this reason, some $S°$ values are negative for aqueous ions—an impossibility for substances.

Tabulated standard molar entropies are used to calculate entropy changes in chemical reactions at 25°C and 1 atm, just as standard enthalpies of formation are combined to obtain enthalpies of reaction according to Hess's law (see Section 12.3).

EXAMPLE 13.9

Using the table of standard molar entropies in Appendix D, calculate $\Delta S°$ for the chemical reaction

$$N_2(g) + 2\ O_2(g) \longrightarrow 2\ NO_2(g)$$

with reactants and products at a temperature of 25°C and a pressure of 1 atm.

SOLUTION

From the table,

$$S°(N_2(g)) = 191.50\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$S°(O_2(g)) = 205.03\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$S°(NO_2(g)) = 239.95\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

The entropy change for the reaction is the sum of the entropies of the products, minus the sum of entropies of the reactants, each multiplied by its coefficient in the balanced chemical equation:

$$\begin{aligned}\Delta S° &= 2S°(NO_2(g)) - S°(N_2(g)) - 2S°(O_2(g))\\ &= (2\ \mathrm{mol})(239.95\ \mathrm{J\ K^{-1}\ mol^{-1}}) - (1\ \mathrm{mol})(191.50\ \mathrm{J\ K^{-1}\ mol^{-1}}) -\\ &\quad (2\ \mathrm{mol})(205.03\ \mathrm{J\ K^{-1}\ mol^{-1}})\\ &= -121.66\ \mathrm{J\ K^{-1}}\end{aligned}$$

The factors of 2 multiply $S°$ for NO_2 and O_2 because 2 mol of each appears in the chemical equation. Note that standard molar entropies, unlike standard molar enthalpies of formation $\Delta H_f°$, are not zero for elements at 25°C. The negative $\Delta S°$ results because this is the entropy change of the system only. The surroundings must undergo a positive entropy change in such a way that $\Delta S_{tot} \geq 0$.

Related Problems: 23, 24, 25, 26

13.7 The Gibbs Free Energy

In Section 13.5, we showed that the change in entropy of a system plus its surroundings (that is, the total change of entropy, ΔS_{tot}) provides a criterion for deciding whether a process is spontaneous, reversible, or impossible:

$$\Delta S_{tot} > 0 \quad \text{spontaneous} \qquad [13.16a]$$

$$\Delta S_{tot} = 0 \quad \text{reversible} \qquad [13.16b]$$

$$\Delta S_{\text{tot}} < 0 \quad \text{nonspontaneous} \qquad [13.16c]$$

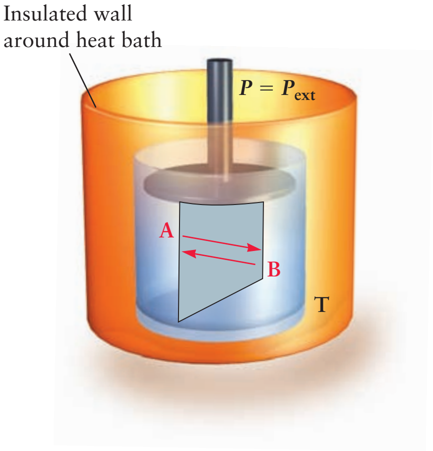


FIGURE 13.9 After the constraint between phases A and B is removed, matter can flow spontaneously between phases inside a system held at constant *T* (temperature) and *P* (pressure) by its surroundings.

Although the algebraic sign of ΔS_{tot} is a completely general criterion for the spontaneity or impossibility of a process, it requires calculating the entropy change for the surroundings, as well as for the system. It would be much more convenient to have a state function that predicts the feasibility of a process in the system without explicit calculations for the surroundings.

For the special case of processes at constant temperature and pressure, the most important in chemistry, such a state function exists. It is called the *Gibbs free energy* and is denoted by G. We start the discussion of G with a qualitative examination of spontaneous laboratory processes at fixed T and P. Then we define G and develop its properties. Finally, we apply ΔG to determine spontaneity in phase transitions and chemical reactions.

Nature of Spontaneous Processes at Fixed *T* and *P*

Consider a system enclosed in a piston-cylinder assembly, which constrains pressure at the value P. The assembly is immersed in a heat bath, which constrains temperature at the value T. Experience shows that spontaneous processes under these conditions consist of spontaneous flow of molecules across a boundary completely internal to the system, separating different regions (called *phases*) of the system (Fig. 13.9).

Under these conditions, we visualize starting a spontaneous process by bringing phases A and B in Figure 13.9 into contact—both already prepared at T and P—but separated by an impermeable membrane (a constraint) that prevents exchange of matter between the phases. Removing the constraint allows spontaneous flow of molecules across the interface between phases. The system does not exchange matter with the surroundings, and the distribution of energy and volume between system and surroundings is not described explicitly. The only function of the surroundings is to maintain T and P constant throughout the experiment. Consequently, as we show in the next subsection, spontaneity of the process is determined by the change in Gibbs free energy of the *system only* while T and P remain constant.

These processes lead to changes in the structure or composition of the phases. Solutes are redistributed between immiscible solvents. Phase transitions occur between the solid, liquid, and gaseous states. Reactants become products. The system may gain or lose heat from the large heat reservoir while these rearrangements occur in its phases, but T remains constant. For example, the latent heat of fusion released during freezing of a liquid in the system is absorbed by the bath. Endothermic processes in the system will take heat from the bath, and exothermic processes will give heat to the bath. P–V work may be done on or by the system at constant P, depending on whether its density increases or decreases through the rearrangements of its phases.

Whether molecules flow spontaneously from phase A to B, or vice versa, is determined by the associated change in Gibbs free energy, as we show in the following subsection.

Gibbs Free Energy and Its Properties

During any process conducted at constant T and P as described earlier, the heat gained by the system is $\Delta H_{\text{sys}} = q_{\text{P}}$ and the heat transferred to the surroundings is $-q_{\text{P}} = -\Delta H_{\text{sys}}$. Because the surroundings remain at constant temperature during the process, the transfer of process heat must have the same effect on them as would a reversible transfer of the same amount of heat. Their entropy change is then

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T_{\text{surr}}}$$

The total entropy change is

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T_{\text{surr}}}$$

$$= \frac{-(\Delta H_{\text{sys}} - T_{\text{surr}}\,\Delta S_{\text{sys}})}{T_{\text{surr}}}$$

Because the temperature, T, is the same for both the system and the surroundings, we can rewrite this as

$$\Delta S_{\text{tot}} = \frac{-\Delta(H_{\text{sys}} - TS_{\text{sys}})}{T} \qquad [13.17]$$

We define the **Gibbs free energy** G as

$$\boxed{G = H - TS} \qquad [13.18]$$

therefore, Equation 13.17 becomes

$$\Delta S_{\text{tot}} = \frac{-\Delta G_{\text{sys}}}{T} \qquad [13.19]$$

Because the absolute temperature T is always positive, ΔS_{tot} and ΔG_{sys} must have the opposite sign for processes occurring at constant T and P. It follows that

$$\boxed{\Delta G_{\text{sys}} < 0 \quad \text{spontaneous processes}} \qquad [13.20a]$$

$$\boxed{\Delta G_{\text{sys}} = 0 \quad \text{reversible processes}} \qquad [13.20b]$$

$$\boxed{\Delta G_{\text{sys}} > 0 \quad \text{nonspontaneous processes}} \qquad [13.20c]$$

for processes conducted at constant temperature and pressure. If $\Delta G_{\text{sys}} > 0$ for a proposed process, then $\Delta G_{\text{sys}} < 0$ for the *reverse* of the proposed process, and that reverse process can occur spontaneously. Experimentally, one prepares the system initially at chosen values of T and P, and then releases the appropriate constraint to allow a process. The resulting "flow" of matter between phases A and B goes in the direction that reduces the value of G for the system, so that $\Delta G < 0$ at the selected values of T and P.

Gibbs Free Energy and Phase Transitions

As a simple application of the Gibbs free energy, consider the freezing of 1 mol liquid water to form ice:

$$H_2O(\ell) \longrightarrow H_2O(s)$$

Let us first examine what thermodynamics predicts when this process occurs at the ordinary freezing point of water under atmospheric pressure, 273.15 K. The measured enthalpy change (the heat absorbed at constant pressure) is

$$\Delta H_{273} = q_P = -6007 \text{ J}$$

At $T_f = 273.15$ K, water freezes reversibly—the system remains close to equilibrium as it freezes. Therefore, the entropy change is

$$\Delta S_{273} = \frac{q_{\text{rev}}}{T_f} = \frac{-6007 \text{ J}}{273.15\ K} = -21.99 \text{ J K}^{-1}$$

The Gibbs free energy change is

$$\Delta G_{273} = \Delta H_{273} - T\,\Delta S_{273} = -6007 \text{ J} - (273.15 \text{ K})(-21.99 \text{ J K}^{-1}) = 0$$

At the normal freezing point, the Gibbs free energy change is zero because the freezing of water under these conditions is an equilibrium, reversible process.

Now, let's see what thermodynamics predicts as the water is cooled below 273.15 to 263.15 K (−10.00°C). Let's calculate the change in Gibbs free energy as water freezes at this lower temperature.

Assume that ΔH and ΔS for the freezing process do not depend on temperature. Then we can write

$$\Delta G_{263} = -6007 \text{ J} - (263.15 \text{ K})(-21.99 \text{ J K}^{-1}) = -220 \text{ J}$$

An exact calculation takes into account that ΔH and ΔS *do* depend slightly on temperature, and it leads to

$$\Delta G_{263} = -213 \text{ J}$$

for the process. Because $\Delta G < 0$, thermodynamics predicts the undercooled water will freeze spontaneously at 263.15 K. At a temperature *higher* than T_f, ΔG is greater than 0, predicting that the liquid would not freeze. This agrees with our experience in nature. Water does not freeze at atmospheric pressure if the temperature is held greater than 273.15 K; instead, the reverse process occurs, and ice melts spontaneously.

Writing the Gibbs free energy change as $\Delta G = \Delta H - T\,\Delta S$ shows that a negative value of ΔG—and therefore a spontaneous process—is favored by a negative value of ΔH and a positive value of ΔS. For freezing a liquid, ΔH is negative, but ΔS for freezing is also negative. Whether a liquid freezes depends on the competition between two factors: an enthalpy change that favors freezing and an entropy change that disfavors freezing (Fig. 13.10). At temperatures less than T_f, the former dominates and the liquid freezes spontaneously, but at temperatures greater than T_f, the latter dominates and freezing does not occur. At T_f, the Gibbs free energies of the two phases are equal ($\Delta G = 0$), and the phases coexist at equilibrium. Similar types of analysis apply to other phase transitions, such as condensing a gas to a liquid.

Gibbs Free Energy and Chemical Reactions

The change in the Gibbs free energy provides a criterion for the spontaneity of any process occurring at constant temperature and pressure (Fig. 13.11). To predict whether a chemical reaction is spontaneous at given values of T and P, it is

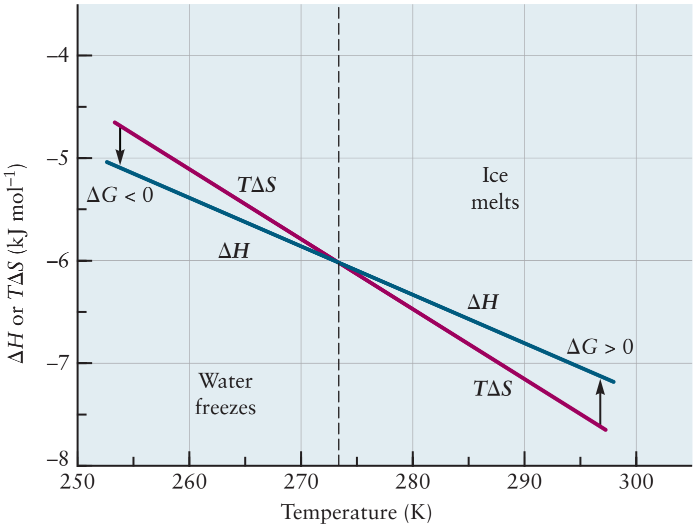


FIGURE 13.10 Plots of ΔH and $T\,\Delta S$ versus temperature for the freezing of water. At 273.15 K, the two curves cross, meaning that at this temperature, $\Delta G = 0$ and ice and water coexist. Below this temperature, the freezing of water to ice is spontaneous; above it, the reverse process, the melting of ice to water, is spontaneous.

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FIGURE 13.11 The dissolution of hydrogen chloride in water, $HCl(g) \longrightarrow HCl(aq)$, is a spontaneous process, with $\Delta G° = -35.9$ kJ. In this demonstration, the upper flask is filled with gaseous hydrogen chloride and a small amount of water is injected into it. As the hydrogen chloride dissolves spontaneously, its pressure declines. The resulting air pressure difference draws water up the tube from the lower flask, allowing more hydrogen chloride to dissolve. The change is so fast that a vigorous fountain of water plays into the upper flask. The free energy change of the process appears as work, raising the water.

necessary to determine only the sign of ΔG for the reaction at these same conditions. From experience with other state functions, we would expect to calculate ΔG for reactions by consulting appropriate tabulations of free energy data. Because we cannot know the absolute value of the Gibbs free energy of a substance (just as we cannot know the absolute value of its internal energy U), it is convenient to define a **standard molar Gibbs free energy of formation,** ΔG_f°, analogous to the standard molar enthalpy of formation ΔH_f° introduced in Section 12.5. From tables of ΔG_f° we can calculate $\Delta G°$ for a wide range of chemical reactions, just as we used Hess's law to calculate $\Delta H°$ for a reaction from tables of ΔH_f° for products and reactants. The next few paragraphs show how tables of ΔG_f° are generated and how the data are used to determine spontaneity of reactions.

STANDARD-STATE FREE ENERGIES The change in the Gibbs free energy for a chemical reaction performed at constant temperature is

$$\Delta G = \Delta H - T\,\Delta S \qquad [13.21]$$

where ΔH is the enthalpy change in the reaction (considered in Section 12.5) and ΔS is the entropy change in the reaction (see Section 13.5). The standard molar Gibbs free energy of formation ΔG_f° of a compound is the change in Gibbs free energy for the reaction in which 1 mol of the compound in its standard state is formed from its elements in their standard states. (You should review the definition of standard states in Section 12.5.) For example, ΔG_f° for $CO_2(g)$ is given by the Gibbs free energy change for the reaction

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta G_f^\circ = ?$$

The value of ΔG_f° can be constructed from Equation 13.21 by using ΔH_f° and $\Delta S°$ values for this reaction and setting $T = 298.15$ K. For this reaction, $\Delta H°$ is simply ΔH_f° for $CO_2(g)$, because graphite and oxygen are elements in their standard states,

$$\Delta H° = \Delta H_f^\circ(CO_2) = -393.51 \text{ kJ}$$

The value of $\Delta S°$ can be obtained from the absolute entropies of the substances involved at 25°C and 1 atm pressure (both elements and compounds, because the absolute entropy $S°$ of an element is not zero in its standard state).

$$\begin{aligned}\Delta S° &= S°(CO_2) - S°(C) - S°(O_2) = 213.63 - 5.74 - 205.03 \text{ J K}^{-1}\\ &= +2.86 \text{ J K}^{-1}\end{aligned}$$

The ΔG_f° for CO_2 is then

$$\begin{aligned}\Delta G_f^\circ &= \Delta H_f^\circ - T\,\Delta S° = -393.51 \text{ kJ} - (298.15 \text{ K})(2.86 \text{ J K}^{-1})(10^{-3} \text{ kJ J}^{-1})\\ &= -394.36 \text{ kJ}\end{aligned}$$

Appendix D includes a table of ΔG_f° values for numerous substances, all obtained by the method just illustrated. Note that our definition makes $\Delta G_f^\circ = 0$ for an *element* that is already in its standard state.

Because G is a state function, chemical equations can be added together—with their ΔG_f° values combined as in Hess's law for changes in enthalpy—to calculate Gibbs free energy changes for chemical reactions under standard-state conditions.

EXAMPLE 13.10

Calculate $\Delta G°$ for the following reaction, using tabulated values for ΔG_f° from Appendix D.

$$3\ NO(g) \longrightarrow N_2O(g) + NO_2(g)$$

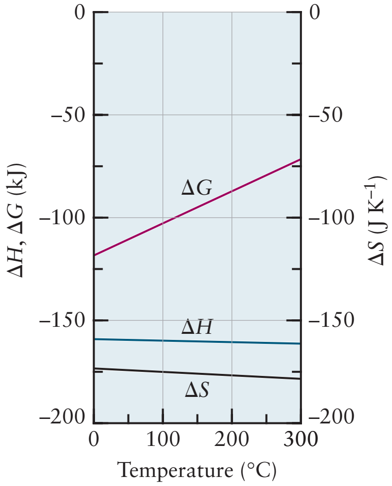


FIGURE 13.12 The entropy change of the reaction 3 $NO(g) \longrightarrow N_2O(g) + NO_2(g)$ varies less than 5% between 0°C and 300°C; the enthalpy of reaction is even closer to constancy. The free energy change in the reaction shifts greatly over the temperature range, however, as the magnitude of $T\,\Delta S$ increases. Note that the units are very different on the left- (energy) and right-hand vertical axes (entropy).

SOLUTION

$$\Delta G° = \Delta G_f°(N_2O) + \Delta G_f°(NO_2) - 3\,\Delta G_f°(NO)$$

$$= (1\text{ mol})(104.18\text{ kJ mol}^{-1}) + (1\text{ mol})(51.29\text{ kJ mol}^{-1}) - (3\text{ mol})(86.55\text{ kJ mol}^{-1})$$

$$= -104.18\text{ kJ}$$

EFFECTS OF TEMPERATURE ON ΔG Values of $\Delta G°$ calculated from the data in Appendix D are accurate only at $T = 298.15$ K. Values of $\Delta G°$ can be estimated for reactions at other temperatures and at $P = 1$ atm using the equation

$$\Delta G° = \Delta H° - T\,\Delta S° \qquad [13.22]$$

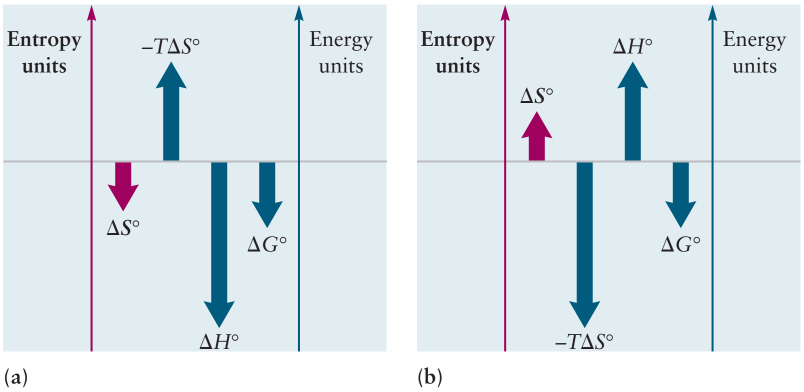
and tables of standard entropies and standard enthalpies of formation. The estimates will be close to the true value if $\Delta H°$ and $\Delta S°$ are not strongly dependent on T, which is usually the case (Fig. 13.12).

The value and the sign of $\Delta G°$ can depend strongly on T, even when the values of $\Delta H°$ and $\Delta S°$ do not, because of the competition between $\Delta H°$ and $T\,\Delta S°$ in Equation 13.22. If $\Delta H°$ is negative and $\Delta S°$ is positive, then the reaction is spontaneous at all temperatures when reactants and products are at atmospheric pressure. If $\Delta H°$ is positive and $\Delta S°$ is negative, the reaction is never spontaneous. For the other possible combinations, there exists a special temperature T^*, defined by

$$T^* = \frac{\Delta H°}{\Delta S°} \qquad [13.23]$$

at which $\Delta G°$ equals zero. If both $\Delta H°$ and $\Delta S°$ are positive, the reaction will be spontaneous at temperatures greater than T^*. If both are negative, the reaction will be spontaneous at temperatures less than T^* (Fig. 13.13). This discussion demonstrates an important result from chemical thermodynamics with enormous practical importance: With knowledge of $\Delta H°$ and $\Delta S°$, we can manipulate conditions to make a reaction spontaneous.

FIGURE 13.13 The competition between $\Delta H°$ and $\Delta S°$ determines the temperature range in which a reaction is spontaneous. (a) If both $\Delta H°$ and $\Delta S°$ are negative, the reaction is spontaneous at temperatures less than $T^* = \Delta H°/\Delta S°$. (b) If both $\Delta H°$ and $\Delta S°$ are positive, the reaction is spontaneous at temperatures greater than $T^* = \Delta H°/\Delta S°$.



CHAPTER SUMMARY

This chapter opened with the quest for methods of predicting whether a chemical reaction can occur spontaneously under a given set of conditions. The second law provides the answer: Any process is spontaneous under conditions where the total entropy of the *system and its surroundings* can increase during the process. For the particular case of constant temperature (T) and pressure (P)—the conditions most widely used for chemical reaction—the second law asserts that any process is spontaneous when the Gibbs free energy of the *system alone* can decrease during the process. The temperature dependence of the Gibbs free energy change shows that with knowledge of $\Delta H°$ and $\Delta S°$, we can identify the temperature range in which a given reaction is spontaneous. From the point of view of chemistry, predicting this temperature range is the most important result from the second law. All other material in this chapter can be viewed as preliminary background for arriving at this one crucial result.

The Gibbs free energy is the thermodynamic state function most naturally suited to describing the progress of chemical reactions at constant T and P. It provides the basis for predicting the equilibrium composition of the reaction mixture in Chapter 14.

CUMULATIVE EXERCISE

Purifying Nickel

Impure nickel, obtained from the smelting of its sulfide ores in a blast furnace, can be converted to metal of 99.90% to 99.99% purity by the Mond process, which relies on the equilibrium

$$\mathrm{Ni}(s) + 4\ \mathrm{CO}(g) \rightleftharpoons \mathrm{Ni(CO)_4}(g)$$

The standard enthalpy of formation of nickel tetracarbonyl, $\mathrm{Ni(CO)_4}(g)$, is $-602.9\ \mathrm{kJ\ mol^{-1}}$, and its absolute entropy $S°$ is $410.6\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

(a) Predict (without referring to a table) whether the entropy change of the system (the reacting atoms and molecules) is positive or negative in this process.

(b) At a temperature where this reaction is spontaneous, predict whether the entropy change of the surroundings is positive or negative.

(c) Use the data in Appendix D to calculate $\Delta H°$ and $\Delta S°$ for this reaction.

(d) At what temperature is $\Delta G° = 0$ for this reaction?

(e) The first step in the Mond process is the equilibration of impure nickel with CO and $\mathrm{Ni(CO)_4}$ at about 50°C. In this step, the goal is to draw as much nickel as possible into the vapor-phase complex. Calculate $\Delta G°$ for the preceding reaction at 50°C.

(f) In the second step of the Mond process, the gases are removed from the reaction chamber and heated to about 230°C. At high enough temperatures, the sign of $\Delta G°$ is reversed and the reaction occurs in the opposite direction, depositing pure nickel. In this step, the goal is to deposit as much nickel as possible from the vapor-phase complex. Calculate $\Delta G°$ for the preceding reaction at 230°C.

(g) The Mond process relies on the volatility of $\mathrm{Ni(CO)_4}$ for its success. Under room conditions, this compound is a liquid, but it boils at 42.2°C with an enthalpy of vaporization of $29.0\ \mathrm{kJ\ mol^{-1}}$. Calculate the entropy of vaporization of $\mathrm{Ni(CO)_4}$, and compare it with that predicted by Trouton's rule.

(h) A recently developed variation of the Mond process carries out the first step at higher pressures and at a temperature of 150°C. Estimate the maximum pressure of $\mathrm{Ni(CO)_4}(g)$ that can be attained before the gas will liquefy at this temperature (that is, calculate the vapor pressure of $\mathrm{Ni(CO)_4}(\ell)$ at 150°C).

Answers

(a) Negative

(b) Positive

(c) $\Delta H° = -160.8$ kJ; $\Delta S° = -409.5$ J K^{-1}

(d) 392.7 K = 119.5°C

(e) $\Delta G° = -28.4$ kJ

(f) $\Delta G° = +46.0$ kJ

(g) 92.0 J K^{-1} mol^{-1}, close to the Trouton's rule value of 88 J K^{-1} mol^{-1}

(h) 16.7 atm

CHAPTER REVIEW

- In general and qualitative terms, a spontaneous process is one that can occur by itself—given enough time—without outside intervention, once conditions have been established for its initiation.
- The outcome of a spontaneous process depends on the rate of the process. If it is slow, considerable time may be required before the results are seen.
- Spontaneous processes are described precisely in the language of thermodynamics. Initially, some barrier or constraint between the system and surroundings prevents their interaction. Once the constraint is removed, the spontaneous process is allowed to begin. During the process, the system may gain or lose energy, matter, and volume in exchange with the surroundings.
- A spontaneous process occurs in that direction which increases the total entropy of the combination system plus surroundings.
- A molecular statistical analysis shows that a spontaneous process occurs in the direction that gives the system access to more microstates. The extremely high probability that the system moves to the conditions with more microstates is a consequence of the large number of molecules in the system.
- In the molecular statistical analysis, Boltzmann defined the entropy S in any thermodynamic state as $S = k_B \ln \Omega$, where Ω is the number of microstates available to the system in that same thermodynamic state. This equation is used for qualitative interpretations of entropy changes. It shows that any process that increases Ω will increase S, and any process that decreases Ω will decrease S.
- By analyzing the Carnot cycle description of macroscopic energy transfer processes, Clausius demonstrated that the quantity $\int(1/T)dq_{rev}$ is a state function, because its value for any reversible process is independent of the path. Based on this result, Clausius defined the procedure for calculating the entropy change $\Delta S = S_f - S_i$ for a system between any thermodynamic states i and f as $\Delta S = \int_i^f (1/T)dq_{rev}$. The integral can be evaluated along any reversible path between i and f so long as T and dq_{rev} are known along the path. Because S is a state function, this procedure is valid for any process—even an irreversible one—that connects states i and f.
- It is easy to calculate entropy changes for isothermal processes, because T is constant and comes outside the integral to give $\Delta S = q_{rev}/T$. A specific example is the isothermal compression or expansion of an ideal gas, for which $\Delta S = nR \ln(V_f/V_i)$. A second example is any phase transition at constant pressure for which $q_{rev} = \Delta H_{trans}$. The entropy change is then $\Delta S_{trans} = \Delta H_{trans}/T_{trans}$.

- When the temperature changes during the process, we account for the variation of T along the process path by writing $dq_{\text{rev}} = nc_X dT$, where X represents V or P for a constant volume or a constant pressure process, respectively. When c_X is constant, the integral gives $\Delta S = nc_X \ln(T_f/T_i)$.
- Usually the surroundings is sufficiently large that it can be considered a constant temperature heat bath during the process. The heat lost by the system during the process is gained by the surroundings, so the entropy change for the surroundings is $\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T_{\text{surr}}$. If the surroundings is not large enough to be treated in this way, ΔS_{surr} is calculated by the same procedures as ΔS_{sys}.
- To determine whether a process is spontaneous, we must calculate the total entropy change, $\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$. If $\Delta S_{\text{tot}} > 0$, the process is spontaneous. If $\Delta S_{\text{tot}} < 0$, the process cannot occur spontaneously. If $\Delta S_{\text{tot}} = 0$, the system is at equilibrium, and no process will occur.
- The third law of thermodynamics states that the entropy of any pure substance in equilibrium approaches zero at the absolute zero of temperature. Consequently, the entropy of every pure substance has a fixed value at each temperature and pressure, which can be calculated by starting with the low-temperature values and adding the results of all phase transitions that occur at intervening temperatures. This leads to tabulations of standard molar entropy $S°$ at 298.15 K and 1 atm pressure, which can be used to calculate entropy changes for chemical reactions in which the reactants and products are in these standard states.
- When processes are conducted at fixed temperature and pressure, spontaneity is determined by changes in the Gibbs free energy, $G = H - TS$, for the system with no consideration of changes in the surroundings. If $\Delta G < 0$, the process is spontaneous. If $\Delta G > 0$, the process cannot occur spontaneously. If $\Delta G = 0$, the system is at equilibrium, and no process will occur.
- Tabulations of the standard Gibbs free energy of formation for each substance in its standard state have been prepared by combining absolute entropy values with standard enthalpy of formation values. We can determine whether any chemical reaction is spontaneous by calculating its value of ΔG from the tabulated standard Gibbs free energy for its reactants and products. The algebraic sign of ΔG tells us whether the reaction is spontaneous.
- Whether a reaction is spontaneous depends on the relation between $\Delta H°$ and $\Delta S°$ at the temperature of the reaction. If $\Delta H° < 0$ and $\Delta S° > 0$, the reaction is spontaneous at all temperatures. If $\Delta H° > 0$ and $\Delta S° < 0$, the reaction is never spontaneous. For other combinations, there is a special temperature $T^* = \Delta H°/\Delta S°$ at which $\Delta G° = 0$. If both $\Delta H°$ and $\Delta S°$ are positive, the reaction is spontaneous for temperatures greater than T^*. If both $\Delta H°$ and $\Delta S°$ are negative, the reaction is spontaneous for temperatures less than T^*.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Identify the system and surroundings involved in a spontaneous process and identify the constraint that was removed to enable the process to occur (Section 13.1, Problems 1–2).
2. Provide a statistical interpretation of the change in entropy that occurs when a gas undergoes a volume change (Section 13.2, Problems 3–10).
3. Summarize the justification that entropy is a state function (Sections 13.3 and 13.4).
4. Calculate the entropy change for the system and the surroundings for reversible and irreversible processes (Section 13.5, Problems 13–22).

5. Describe measurements of absolute entropy, and calculate standard-state entropy changes for chemical reactions (Section 13.6, Problems 23–30).
6. Define the Gibbs free energy function and state the criterion it provides for the spontaneity of a process (Section 13.7).
7. Calculate the change in Gibbs free energy for reversible and spontaneous phase transformations (Section 13.7, Problems 31–34).
8. Calculate the change in Gibbs free energy for chemical reactions and identify temperature ranges in which a particular reaction is spontaneous (Section 13.7, Problems 35–40).

KEY EQUATIONS

$S = k_B \ln \Omega$ **(Section 13.2)**

$w_{net} = -nR(T_h - T_l) \ln \frac{V_B}{V_A}$ **(Section 13.4)**

$\epsilon = \frac{-w_{net}}{q_h} = \frac{T_h - T_l}{T_h}$ **(Section 13.4)**

$\frac{q_h}{T_h} + \frac{q_l}{T_l} = 0$ **(Section 13.4)**

$\Delta S = \int_i^f \frac{dq_{rev}}{T}$ **(Section 13.4)**

$\Delta S = \int_i^f \frac{dq_{rev}}{T} = \frac{1}{T}\int_i^f dq_{rev} = \frac{q_{rev}}{T}$ (constant T) **(Section 13.5)**

$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$ (constant T) **(Section 13.5)**

$\Delta S_{fus} = \frac{q_{rev}}{T_f} = \frac{\Delta H_{fus}}{T_f}$ **(Section 13.5)**

$\Delta S_{vap} = 88 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$ **(Section 13.5)**

$\Delta S = \int_{T_1}^{T_2} \frac{nc_V}{T} dT = nc_V \ln\left(\frac{T_2}{T_1}\right)$ (constant V) **(Section 13.5)**

$\Delta S = \int_{T_1}^{T_2} \frac{nc_P}{T} dT = nc_P \ln\left(\frac{T_2}{T_1}\right)$ (constant P) **(Section 13.5)**

$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T_{surr}}$ **(Section 13.5)**

$S° = \int_0^{298.15} \frac{c_P}{T} dT + \Delta S$ (phase changes between 0 and 298.15 K) **(Section 13.6)**

$\Delta S_{tot} > 0$ spontaneous **(Section 13.7)**

$\Delta S_{tot} = 0$ reversible **(Section 13.7)**

$\Delta S_{tot} < 0$ impossible **(Section 13.7)**

$G = H - TS$ **(Section 13.7)**

$\Delta G_{sys} < 0$ spontaneous processes **(Section 13.7)**

$\Delta G_{\text{sys}} = 0$ reversible processes (Section 13.7)

$\Delta G_{\text{sys}} > 0$ nonspontaneous processes (Section 13.7)

$\Delta G = \Delta H - T\,\Delta S$ (Section 13.7)

$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$ (Section 13.7)

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

The Nature of Spontaneous Processes

1. For each of the following processes, identify the system and the surroundings. Identify those processes that are spontaneous. For each spontaneous process, identify the constraint that has been removed to enable the process to occur:
 (a) Ammonium nitrate dissolves in water.
 (b) Hydrogen and oxygen explode in a closed bomb.
 (c) A rubber band is rapidly extended by a hanging weight.
 (d) The gas in a chamber is slowly compressed by a weighted piston.
 (e) A glass shatters on the floor.

2. For each of the following processes, identify the system and the surroundings. Identify those processes that are spontaneous. For each spontaneous process, identify the constraint that has been removed to enable the process to occur:
 (a) A solution of hydrochloric acid is titrated with a solution of sodium hydroxide.
 (b) Zinc pellets dissolve in aqueous hydrochloric acid.
 (c) A rubber band is slowly extended by a hanging weight.
 (d) The gas in a chamber is rapidly compressed by a weighted piston.
 (e) A tray of water freezes in the freezing compartment of an electric refrigerator.

Entropy and Spontaneity: A Molecular Statistical Interpretation

3. (a) How many "microstates" are there for the numbers that come up on a pair of dice?
 (b) What is the probability that a roll of a pair of dice will show two sixes?

4. (a) Suppose a volume is divided into three equal parts. How many microstates can be written for all possible ways of distributing four molecules among the three parts?
 (b) What is the probability that all four molecules are in the leftmost third of the volume at the same time?

5. When $H_2O(\ell)$ and $D_2O(\ell)$ are mixed, the following reaction occurs spontaneously:

$$H_2O(\ell) + D_2O(\ell) \rightarrow 2\ HOD(\ell)$$

There is little difference between the enthalpy of an O—H bond and that of an O—D bond. What is the main driving force for this reaction?

6. The two gases $BF_3(g)$ and $BCl_3(g)$ are mixed in equal molar amounts. All B—F bonds have about the same bond enthalpy, as do all B—Cl bonds. Explain why the mixture tends to react to form $BF_2Cl(g)$ and $BCl_2F(g)$.

7. Two large glass bulbs of identical volume are connected by means of a stopcock. One bulb initially contains 1.00 mol H_2; the other contains 1.00 mol helium (He). The stopcock is opened and the gases are allowed to mix and reach equilibrium. What is the probability that all the H_2 in the first bulb will diffuse into the second bulb and all the He gas in the second bulb will diffuse into the first bulb?

8. A mixture of 2.00 mol nitrogen and 1.00 mol oxygen is in thermal equilibrium in a 100-L container at 25°C. Calculate the probability that at a given time all the nitrogen will be found in the left half of the container and all the oxygen in the right half.

9. Predict the sign of the system's entropy change in each of the following processes.
 (a) Sodium chloride melts
 (b) A building is demolished
 (c) A volume of air is divided into three separate volumes of nitrogen, oxygen, and argon, each at the same pressure and temperature as the original air

10. Predict the sign of the system's entropy change in each of the following processes.
 (a) A computer is constructed from iron, copper, carbon, silicon, gallium, and arsenic
 (b) A container holding a compressed gas develops a leak and the gas enters the atmosphere
 (c) Solid carbon dioxide (dry ice) sublimes to gaseous carbon dioxide

A DEEPER LOOK . . . Carnot Cycles, Efficiency, and Entropy

11. A thermodynamic engine operates cyclically and reversibly between two temperature reservoirs, absorbing heat from the high-temperature bath at 450 K and discharging heat to the low-temperature bath at 300 K.
 (a) What is the thermodynamic efficiency of the engine?
 (b) How much heat is discarded to the low-temperature bath if 1500 J of heat is absorbed from the high-temperature bath during each cycle?
 (c) How much work does the engine perform in one cycle of operation?

12. In each cycle of its operation, a thermal engine absorbs 1000 J of heat from a large heat reservoir at 400 K and discharges heat to another large heat sink at 300 K. Calculate:

- (a) The thermodynamic efficiency of the heat engine, operated reversibly
- (b) The quantity of heat discharged to the low-temperature sink each cycle
- (c) The maximum amount of work the engine can perform each cycle

Entropy Changes and Spontaneity

13. Tungsten melts at 3410°C and has an enthalpy change of fusion of 35.4 kJ mol^{-1}. Calculate the entropy of fusion of tungsten.

14. Tetraphenylgermane, $(C_6H_5)_4Ge$, has a melting point of 232.5°C, and its enthalpy increases by 106.7 J g^{-1} during fusion. Calculate the molar enthalpy of fusion and molar entropy of fusion of tetraphenylgermane.

15. The normal boiling point of acetone is 56.2°C. Use Trouton's rule to estimate its molar enthalpy of vaporization.

16. The molar enthalpy of vaporization of liquid hydrogen chloride is 16.15 kJ mol^{-1}. Use Trouton's rule to estimate its normal boiling point.

17. If 4.00 mol hydrogen ($c_P = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$) is expanded reversibly and isothermally at 400 K from an initial volume of 12.0 L to a final volume of 30.0 L, calculate ΔU, q, w, ΔH, and ΔS for the gas.

18. Suppose 60.0 g hydrogen bromide, HBr(g), is heated reversibly from 300 to 500 K at a constant volume of 50.0 L, and then allowed to expand isothermally and reversibly until the original pressure is reached. Using $c_P(\text{HBr}(g)) = 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate ΔU, q, w, ΔH, and ΔS for this process. Assume that HBr is an ideal gas under these conditions.

19. Exactly 1 mol ice is heated reversibly at atmospheric pressure from −20°C to 0°C, melted reversibly at 0°C, and then heated reversibly at atmospheric pressure to 20°C. $\Delta H_{\text{fus}} = 6007 \text{ J mol}^{-1}$; $c_P(\text{ice}) = 38 \text{ J K}^{-1} \text{ mol}^{-1}$; and $c_P(\text{water}) = 75 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate ΔS for the system, the surroundings, and the thermodynamic universe for this process.

20. Suppose 1.00 mol water at 25°C is flash-evaporated by allowing it to fall into an iron crucible maintained at 150°C. Calculate ΔS for the water, ΔS for the iron crucible, and ΔS_{tot}, if $c_P(H_2O(\ell)) = 75.4 \text{ J K}^{-1} \text{ mol}^{-1}$ and $c_P(H_2O(g)) = 36.0 \text{ J K}^{-1} \text{ mol}^{-1}$. Take $\Delta H_{\text{vap}} = 40.68 \text{ kJ mol}^{-1}$ for water at its boiling point of 100°C.

21. In Example 12.3, a process was considered in which 72.4 g iron initially at 100.0°C was added to 100.0 g water initially at 10.0°C, and an equilibrium temperature of 16.5°C was reached. Take $c_P(\text{Fe})$ to be 25.1 $\text{J K}^{-1} \text{ mol}^{-1}$ and $c_P(H_2O)$ to be 75.3 $\text{J K}^{-1} \text{ mol}^{-1}$, independent of temperature. Calculate ΔS for the iron, ΔS for the water, and ΔS_{tot} in this process.

22. Iron has a heat capacity of 25.1 $\text{J K}^{-1} \text{ mol}^{-1}$, approximately independent of temperature between 0°C and 100°C.

- (a) Calculate the enthalpy and entropy change of 1.00 mol iron as it is cooled at atmospheric pressure from 100°C to 0°C.
- (b) A piece of iron weighing 55.85 g and at 100°C is placed in a large reservoir of water held at 0°C. It cools irreversibly until its temperature equals that of the water. Assuming the water reservoir is large enough that its temperature remains close to 0°C, calculate the entropy changes for the iron and the water and the total entropy change in this process.

The Third Law of Thermodynamics

23. (a) Use data from Appendix D to calculate the standard entropy change at 25°C for the reaction.

$$N_2H_4(\ell) + 3\ O_2(g) \longrightarrow NO_2(g) + 2\ H_2O(\ell)$$

(b) Suppose the hydrazine (N_2H_4) is in the gaseous, rather than liquid, state. Will the entropy change for its reaction with oxygen be higher or lower than that calculated in part (a)? (*Hint:* Entropies of reaction can be added when chemical equations are added, in the same way that Hess's law allows enthalpies to be added.)

24. (a) Use data from Appendix D to calculate the standard entropy change at 25°C for the reaction.

$$CH_3COOH(g) + NH_3(g) \longrightarrow CH_3NH_2(g) + CO_2(g) + H_2(g)$$

(b) Suppose that 1.00 mol each of solid acetamide, $CH_3CONH_2(s)$, and water, $H_2O(\ell)$, react to give the same products. Will the standard entropy change be larger or smaller than that calculated for the reaction in part (a)?

25. The alkali metals react with chlorine to give salts:

$$2\ Li(s) + Cl_2(g) \longrightarrow 2\ LiCl(s)$$

$$2\ Na(s) + Cl_2(g) \longrightarrow 2\ NaCl(s)$$

$$2\ K(s) + Cl_2(g) \longrightarrow 2\ KCl(s)$$

$$2\ Rb(s) + Cl_2(g) \longrightarrow 2\ RbCl(s)$$

$$2\ Cs(s) + Cl_2(g) \longrightarrow 2\ CsCl(s)$$

Using the data in Appendix D, compute $\Delta S°$ of each reaction and identify a periodic trend, if any.

26. All of the halogens react directly with $H_2(g)$ to give binary compounds. The reactions are

$$F_2(g) + H_2(g) \longrightarrow 2\ HF(g)$$

$$Cl_2(g) + H_2(g) \longrightarrow 2\ HCl(g)$$

$$Br_2(g) + H_2(g) \longrightarrow 2\ HBr(g)$$

$$I_2(g) + H_2(g) \longrightarrow 2\ HI(g)$$

Using the data in Appendix D, compute $\Delta S°$ of each reaction and identify a periodic trend, if any.

27. The dissolution of calcium chloride in water

$$CaCl_2(s) \longrightarrow Ca^{2+}(aq) + 2\ Cl^{-}(aq)$$

is a spontaneous process at 25°C, even though the standard entropy change of the preceding reaction is negative ($\Delta S° = -44.7 \text{ J K}^{-1}$). What conclusion can you draw about the change in entropy of the surroundings in this process?

28. Quartz, $SiO_2(s)$, does not spontaneously decompose to silicon and oxygen at 25°C in the reaction

$$SiO_2(s) \longrightarrow Si(s) + O_2(g)$$

even though the standard entropy change of the reaction is large and positive ($\Delta S° = +182.02\ J\ K^{-1}$). Explain.

29. Use the microscopic interpretation of entropy from Section 13.2 to explain why the entropy change of the system in Problem 28 is positive.

30. (a) Why is the entropy change of the system negative for the reaction in Problem 27, when the ions become dispersed through a large volume of solution? (*Hint:* Think about the role of the solvent, water.)
(b) Use Appendix D to calculate $\Delta S°$ for the corresponding dissolution of $CaF_2(s)$. Explain why this value is even more negative than that given in Problem 27.

The Gibbs Free Energy

31. The molar enthalpy of fusion of solid ammonia is 5.65 kJ mol^{-1}, and the molar entropy of fusion is 28.9 J K^{-1} mol^{-1}.
(a) Calculate the Gibbs free energy change for the melting of 1.00 mol ammonia at 170 K.
(b) Calculate the Gibbs free energy change for the conversion of 3.60 mol solid ammonia to liquid ammonia at 170 K.
(c) Will ammonia melt spontaneously at 170 K?
(d) At what temperature are solid and liquid ammonia in equilibrium at a pressure of 1 atm?

32. Solid tin exists in two forms: white and gray. For the transformation

$$Sn(s, \text{white}) \longrightarrow Sn(s, \text{gray})$$

the enthalpy change is −2.1 kJ and the entropy change is $-7.4\ J\ K^{-1}$.
(a) Calculate the Gibbs free energy change for the conversion of 1.00 mol white tin to gray tin at −30°C.
(b) Calculate the Gibbs free energy change for the conversion of 2.50 mol white tin to gray tin at −30°C.
(c) Will white tin convert spontaneously to gray tin at −30°C?
(d) At what temperature are white and gray tin in equilibrium at a pressure of 1 atm?

33. Ethanol's enthalpy of vaporization is 38.7 kJ mol^{-1} at its normal boiling point, 78°C. Calculate q, w, ΔU, ΔS_{sys}, and ΔG when 1.00 mol ethanol is vaporized reversibly at 78°C and 1 atm. Assume that the vapor is an ideal gas and neglect the volume of liquid ethanol relative to that of its vapor.

34. Suppose 1.00 mol superheated ice melts to liquid water at 25°C. Assume the specific heats of ice and liquid water have the same value and are independent of temperature. The enthalpy change for the melting of ice at 0°C is 6007 J mol^{-1}. Calculate ΔH, ΔS_{sys}, and ΔG for this process.

35. At 1200°C, the reduction of iron oxide to elemental iron and oxygen is not spontaneous:

$$2\ Fe_2O_3(s) \longrightarrow 4\ Fe(s) + 3\ O_2(g) \qquad \Delta G = +840\ kJ$$

Show how this process can be made to proceed if all the oxygen generated reacts with carbon:

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta G = -400\ kJ$$

This observation is the basis for the smelting of iron ore with coke to extract metallic iron.

36. The primary medium for free energy storage in living cells is adenosine triphosphate (ATP). Its formation from adenosine diphosphate (ADP) is not spontaneous:

$$ADP^{3-}(aq) + HPO_4^{2-}(aq) + H^+(aq) \longrightarrow ATP^{4-}(aq) + H_2O(\ell) \quad \Delta G = +34.5\ kJ$$

Cells couple ATP production with the metabolism of glucose (a sugar):

$$C_6H_{12}O_6(aq) + 6\ O_2(g) \longrightarrow 6\ CO_2(g) + 6\ H_2O(\ell) \quad \Delta G = -2872\ kJ$$

The reaction of 1 molecule of glucose leads to the formation of 38 molecules of ATP from ADP. Show how the coupling makes this reaction spontaneous. What fraction of the free energy released in the oxidation of glucose is stored in the ATP?

37. A process at constant T and P can be described as spontaneous if $\Delta G < 0$ and nonspontaneous if $\Delta G > 0$. Over what range of temperatures is each of the following processes spontaneous? Assume that all gases are at a pressure of 1 atm. (*Hint:* Use Appendix D to calculate ΔH and ΔS [assumed independent of temperature and equal to $\Delta H°$ and $\Delta S°$, respectively], and then use the definition of ΔG.)
(a) The rusting of iron, a complex reaction that can be approximated as

$$4\ Fe(s) + 3\ O_2(g) \longrightarrow 2\ Fe_2O_3(s)$$

(b) The preparation of $SO_3(g)$ from $SO_2(g)$, a step in the manufacture of sulfuric acid:

$$SO_2(g) + \tfrac{1}{2}\ O_2(g) \longrightarrow SO_3(g)$$

(c) The production of the anesthetic dinitrogen oxide through the decomposition of ammonium nitrate:

$$NH_4NO_3(s) \longrightarrow N_2O(g) + 2\ H_2O(g)$$

38. Follow the same procedure used in Problem 37 to determine the range of temperatures over which each of the following processes is spontaneous.
(a) The preparation of the poisonous gas phosgene:

$$CO(g) + Cl_2(g) \longrightarrow COCl_2(g)$$

(b) The laboratory-scale production of oxygen from the decomposition of potassium chlorate:

$$2\ KClO_3(s) \longrightarrow 2\ KCl(s) + 3\ O_2(g)$$

(c) The reduction of iron(II) oxide (wüstite) by coke (carbon), a step in the production of iron in a blast furnace:

$$FeO(s) + C(s, gr) \longrightarrow Fe(s) + CO(g)$$

39. Explain how it is possible to reduce tungsten(VI) oxide (WO_3) to metal with hydrogen at an elevated temperature. Over what temperature range is this reaction spontaneous? Use the data of Appendix D.

40. Tungsten(VI) oxide can also be reduced to tungsten by heating it with carbon in an electric furnace:

$$2\ WO_3(s) + 3\ C(s) \longrightarrow 2\ W(s) + 3\ CO_2(g)$$

(a) Calculate the standard free energy change ($\Delta G°$) for this reaction, and comment on the feasibility of the process at room conditions.

(b) What must be done to make the process thermodynamically feasible, assuming ΔH and ΔS are nearly independent of temperature?

ADDITIONAL PROBLEMS

41. Ethanol (CH_3CH_2OH) has a normal boiling point of 78.4°C and a molar enthalpy of vaporization of 38.74 kJ mol^{-1}. Calculate the molar entropy of vaporization of ethanol and compare it with the prediction of Trouton's rule.

42. A quantity of ice is mixed with a quantity of hot water in a sealed, rigid, insulated container. The insulation prevents heat exchange between the ice–water mixture and the surroundings. The contents of the container soon reach equilibrium. State whether the total *internal energy* of the contents decreases, remains the same, or increases in this process. Make a similar statement about the total *entropy* of the contents. Explain your answers.

43. (a) If 2.60 mol $O_2(g)$ (c_P = 29.4 J K^{-1} mol^{-1}) is compressed reversibly and adiabatically from an initial pressure of 1.00 atm and 300 K to a final pressure of 8.00 atm, calculate ΔS for the gas.

(b) Suppose a different path from that in part (a) is used. The gas is first heated at constant pressure to the same final temperature, and then compressed reversibly and isothermally to the same final pressure. Calculate ΔS for this path and show that it is equal to that found in part (a).

44. One mole of a monatomic ideal gas begins in a state with $P = 1.00$ atm and $T = 300$ K. It is expanded reversibly and adiabatically until the volume has doubled; then it is expanded irreversibly and isothermally into a vacuum until the volume has doubled again; and then it is heated reversibly at constant volume to 400 K. Finally, it is compressed reversibly and isothermally until a final state with $P = 1.00$ atm and $T = 400$ K is reached. Calculate ΔS_{sys} for this process. (*Hint:* There are two ways to solve this problem—an easy way and a hard way.)

* 45. The motion of air masses through the atmosphere can be approximated as adiabatic (because air is a poor conductor of heat) and reversible (because pressure differences in the atmosphere are small). To a good approximation, air can be treated as an ideal gas with average molar mass 29 g mol^{-1} and average heat capacity 29 J K^{-1} mol^{-1}.

(a) Show that the displacement of the air masses occurs at constant entropy ($\Delta S = 0$).

(b) Suppose the average atmospheric pressure near the earth's surface is P_0 and the temperature is T_0. The air is displaced upward until its temperature is T and its pressure is P. Determine the relation between P and T. (*Hint:* Consider the process as occurring in two steps: first a cooling from T_0 to T at constant pressure, and then an expansion from P_0 to P at constant temperature. Equate the sum of the two entropy changes to $\Delta S_{tot} = 0$.)

(c) In the lower atmosphere, the dependence of pressure on height, h, above the earth's surface can be approximated as

$$\ln (P/P_0) = -\mathcal{M}gh/RT$$

where $\mathcal{M}$ is the molar mass (kg mol^{-1}), g the acceleration due to gravity (9.8 m s^{-2}), and R the gas constant. If the air temperature at sea level near the equator is 38°C (~100°F), calculate the air temperature at the summit of Mount Kilimanjaro, 5.9 km above sea level. (For further discussion of this problem, see L. K. Nash, *J. Chem. Educ.* 61:23, 1984.)

46. Calculate the entropy change that results from mixing 54.0 g water at 273 K with 27.0 g water at 373 K in a vessel whose walls are perfectly insulated from the surroundings. Consider the specific heat of water to be constant over the temperature range from 273 to 373 K and to have the value 4.18 J K^{-1} g^{-1}.

47. Problem 22 asked for the entropy change when a piece of iron is cooled by immersion in a reservoir of water at 0°C.

(a) Repeat Problem 22(b), supposing that the iron is cooled to 50°C in a large water reservoir held at that temperature before being placed in the 0°C reservoir.

(b) Repeat the calculation supposing that four water reservoirs at 75°C, 50°C, 25°C, and 0°C are used.

(c) As more reservoirs are used, what happens to ΔS for the iron, for the water, and for the universe? How would you attempt to conduct a reversible cooling of the iron?

48. Problem 42 in Chapter 9 described an optical atomic trap. In one experiment, a gas of 500 sodium atoms is confined in a volume of 1000 μm^3. The temperature of the system is 0.00024 K. Compute the probability that, by chance, these 500 slowly moving sodium atoms will all congregate in the left half of the available volume. Express your answer in scientific notation.

* 49. Suppose we have several different ideal gases, $i = 1, 2, 3, \ldots, N$, each occupying its own volume V_i, all at the same pressure and temperature. The boundaries between the volumes are removed so that the gases mix at constant temperature in the total volume $V = \Sigma_i V_i$.

(a) Using the microscopic interpretation of entropy, show that

$$\Delta S = -nR \sum_i X_i \ln X_i$$

for this process, where n is the total number of moles of gas and X_i is the mole fraction of gas i.

(b) Calculate the entropy change when 50 g each of $O_2(g)$, $N_2(g)$, and $Ar(g)$ are mixed at 1 atm and 0°C.

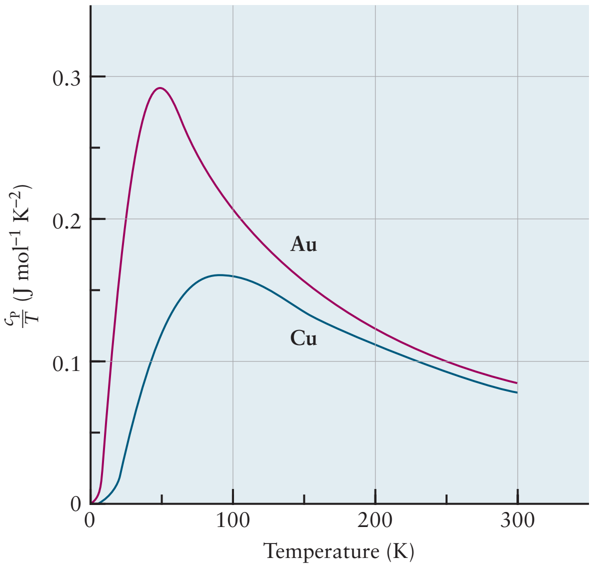
(c) Using Table 9.1, calculate the entropy change when 100 L of air (assumed to be a mixture of ideal gases) at 1 atm and 25°C is separated into its component gases at the same pressure and temperature.

* 50. The N_2O molecule has the structure N—N—O. In an ordered crystal of N_2O, the molecules are lined up in a regular fashion, with the orientation of each determined by its position in the crystal. In a random crystal (formed on rapid freezing), each molecule has two equally likely orientations.

(a) Calculate the number of microstates available to a random crystal of N_A (Avogadro's number) of molecules.

(b) Calculate the entropy change when 1.00 mol of a random crystal is converted to an ordered crystal.

51. By examining the following graphs, predict which element—copper or gold—has the higher absolute entropy at a temperature of 200 K.



* 52. Consider the process described in Problem 19 in Chapter 12. Use the results from that problem to do the following.
(a) Calculate ΔS for the system, the surroundings, and the universe.
(b) If the absolute entropy per mole of the gas *before* the expansion is 158.2 J K^{-1} mol^{-1}, calculate ΔG_{sys} for the process.

53. Two different crystalline forms of sulfur are the rhombic form and the monoclinic form. At atmospheric pressure, rhombic sulfur undergoes a transition to monoclinic when it is heated above 368.5 K:

$$\text{S}(s, \text{rhombic}) \longrightarrow \text{S}(s, \text{monoclinic})$$

(a) What is the sign of the entropy change (ΔS) for this transition?
(b) $|\Delta H|$ for this transition is 400 J mol^{-1}. Calculate ΔS for the transition.

* 54. Use data from Appendix D to estimate the temperature at which $I_2(g)$ and $I_2(s)$ are in equilibrium at a pressure of 1 atm. Can this equilibrium actually be achieved? Refer to Appendix F for data on iodine.

55. The molar enthalpy of fusion of ice at 0°C is 6.02 kJ mol^{-1}; the molar heat capacity of undercooled water is 75.3 J mol^{-1} K^{-1}. (a) One mole of undercooled water at −10°C is induced to crystallize in a heat-insulated vessel. The result is a mixture of ice and water at 0°C. What fraction of this mixture is ice? (b) Calculate ΔS for the system.

56. A certain substance consists of two modifications A and B; $\Delta G°$ for the transition from A to B is positive. The two modifications produce the same vapor. Which has the higher vapor pressure? Which is the more soluble in a solvent common to both?

57. From the values in Appendix D, calculate the values of $\Delta G°$ and $\Delta H°$ for the reaction.

$$3\,\text{Fe}_2\text{O}_3(s) \longrightarrow 2\,\text{Fe}_3\text{O}_4(s) + \tfrac{1}{2}\,\text{O}_2(g)$$

at 25°C. Which of the two oxides is more stable at 25°C and P_{O_2} = 1 atm?

58. The strongest known chemical bond is that in carbon monoxide, CO, with bond enthalpy of 1.05 × 10^3 kJ mol^{-1}. Furthermore, the entropy increase in a gaseous dissociation of the kind AB $\rightleftarrows$ A + B is about 110 J mol^{-1} K^{-1}. These factors establish a temperature above which there is essentially no chemistry of molecules. Show why this is so, and find the temperature.

59. The $\Delta G_f°$ of $Si_3N_4(s)$ is −642.6 kJ mol^{-1}. Use this fact and the data in Appendix D to compute $\Delta G°$ of the reaction.

$$3\,\text{CO}_2(g) + \text{Si}_3\text{N}_4(s) \longrightarrow 3\,\text{SiO}_2(\text{quartz}) + 2\,\text{N}_2(g) + 3\,\text{C}(s, \text{gr})$$

60. The compound $Pt(NH_3)_2I_2$ comes in two forms, the cis and the trans, which differ in their molecular structure. The following data are available:

	$\Delta H_f°$ (kJ mol^{-1})	**$\Delta G_f°$ (kJ mol^{-1})**
cis	−286.56	−130.25
trans	−316.94	−161.50

Combine these data with data from Appendix D to compute the standard entropies ($S°$) of both of these compounds at 25°C.

61. (a) Use data from Appendix D to calculate $\Delta H°$ and $\Delta S°$ at 25°C for the reaction

$$2\,\text{CuCl}_2(s) \rightleftharpoons 2\,\text{CuCl}(s) + \text{Cl}_2(g)$$

(b) Calculate ΔG at 590 K, assuming $\Delta H°$ and $\Delta S°$ are independent of temperature.
(c) Careful high-temperature measurements show that when this reaction is performed at 590 K, ΔH_{590} is 158.36 kJ and ΔS_{590} is 177.74 J K^{-1}. Use these facts to compute an improved value of ΔG_{590} for this reaction. Determine the percentage error in ΔG_{590} that comes from using the 298-K values in place of 590-K values in this case.

62. (a) The normal boiling point of carbon tetrachloride (CCl_4) is 76.5°C. A student looks up the standard enthalpies of formation of $CCl_4(\ell)$ and of $CCl_4(g)$ in Appendix D. They are listed as −135.44 and −102.9 kJ mol^{-1}, respectively. By subtracting the first from the second, she computes $\Delta H°$ for the vaporization of CCl_4 to be 32.5 kJ mol^{-1}. But Table 7.2 states that the ΔH_{vap} of CCl_4 is 30.0 kJ mol^{-1}. Explain the discrepancy.
(b) Calculate the molar entropy change of vaporization (ΔS_{vap}) of CCl_4 at 76.5°C.

63. The typical potassium ion concentration in the fluid outside a cell is 0.0050 M, whereas that inside a muscle cell is 0.15 M.
(a) What is the spontaneous direction of motion of ions through the cell wall?
(b) In *active transport,* cells use free energy stored in ATP (see Problem 36) to move ions in the direction opposite their spontaneous direction of flow. Calculate the cost in free energy to move 1.00 mol K^+ through the cell wall by active transport. Assume no change in K^+ concentrations during this process.

CUMULATIVE PROBLEMS

64. When a gas undergoes a reversible adiabatic expansion, its entropy remains constant even though the volume increases. Explain how this can be consistent with the microscopic interpretation of entropy developed in Section 13.2. (*Hint:* Consider what happens to the distribution of velocities in the gas.)

65. The normal boiling point of liquid ammonia is 240 K; the enthalpy of vaporization at that temperature is 23.4 kJ mol^{-1}. The heat capacity of gaseous ammonia at constant pressure is 38 J mol^{-1} K^{-1}.

    (a) Calculate q, w, ΔH, and ΔU for the following change in state:

    $$2.00 \text{ mol } NH_3(\ell, 1 \text{ atm}, 240 \text{ K}) \longrightarrow$$
    $$2.00 \text{ mol } NH_3(g, 1 \text{ atm}, 298 \text{ K})$$

    Assume that the gas behaves ideally and that the volume occupied by the liquid is negligible.

    (b) Calculate the entropy of vaporization of NH_3 at 240 K.

CHAPTER 14

Chemical Equilibrium

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Gaseous ammonia, NH_3, and gaseous hydrogen chloride, HCl, react to form solid NH_4Cl, the white smoke. In the reverse reaction, solid NH_4Cl decomposes when heated to form gaseous NH_3 and HCl.

Every time we carry out a chemical reaction—from fundamental research studies to practical industrial applications—the *yield* of the reaction is extremely important. Did we obtain all the product we could expect? Chapter 2 shows how to calculate the amount of product expected when we start a reaction with particular amounts of the reactants. This calculation assumes that the reaction goes to completion—that is, all of the limiting reagent is consumed. The resulting number, called the theoretical yield, represents the maximum amount of product that could be obtained from that reaction.

In practice, many reactions do not go to completion but rather approach a state or position of **equilibrium.** This equilibrium position, at which the reaction apparently comes to an end, is a mixture of products and unconsumed reactants present in fixed relative amounts. Once equilibrium has been achieved, there is no further net conversion of reactants to products unless the experimental conditions of the reaction (temperature and pressure) are changed. The equilibrium state is characterized by the **equilibrium constant,** which has a unique value for each reaction. Knowing the equilibrium constant and the initial amounts of reactants and products, we can calculate the composition of the equilibrium reaction mixture. Knowing the equilibrium constant and its dependence on experimental conditions, we can manipulate conditions to maximize the practical yield of that reaction. Calculating the equilibrium composition for a particular reaction and its dependence on experimental conditions is therefore a practical skill of enormous importance in chemistry.

In this chapter we describe the equilibrium constant, its dependence on conditions, and its role in manipulating the yield of reactions, emphasizing those aspects broadly applicable to all chemical reactions. We illustrate these general principles with applications to reactions in the gas phase and to heterogeneous reactions. Detailed applications to reactions in aqueous solutions and electrochemical reactions are presented in the three following chapters.

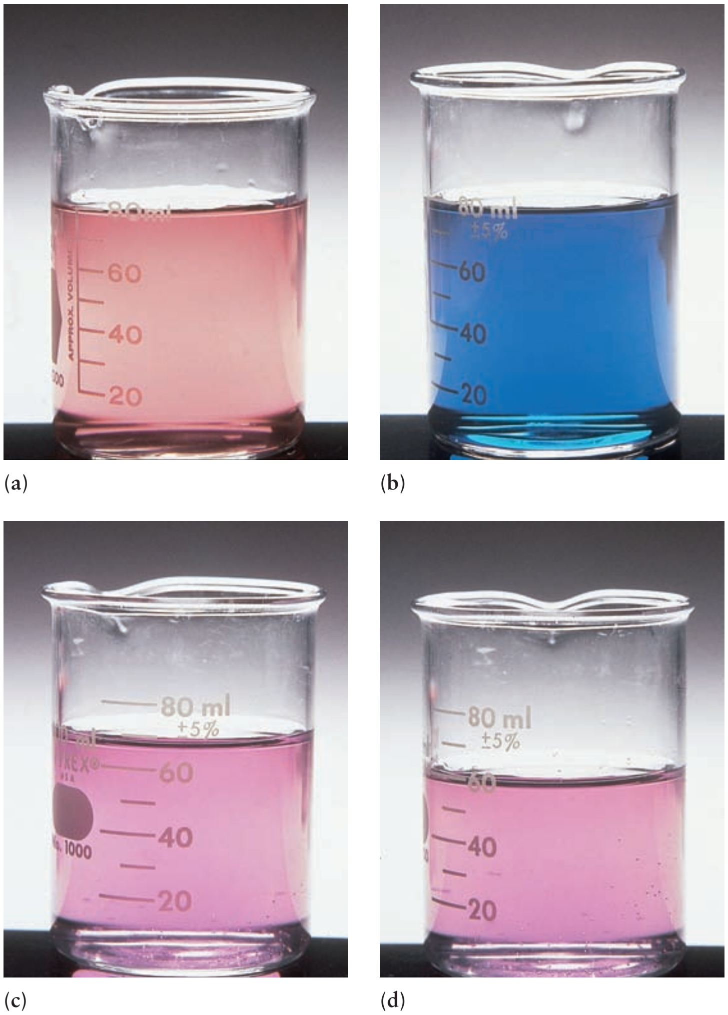
The fact that reactions go to the equilibrium position was discovered empirically, and the equilibrium constant was first defined empirically. All the aforementioned applications can be accomplished with empirically determined equilibrium constants. Nonetheless, the empirical approach leaves unanswered several important fundamental questions: Why should the equilibrium state exist? Why does the equilibrium constant take its particular mathematical form? These and related questions are answered by recognizing that the chemical equilibrium position is the *thermodynamic equilibrium state* of the reaction mixture. Once we have made that connection, thermodynamics explains the existence and the mathematical form of the equilibrium constant. Thermodynamics also gives procedures for calculating the value of the equilibrium constant from the thermochemical properties of the pure reactants and products, as well as procedures for predicting its dependence on experimental conditions.

Some instructors prefer to introduce equilibrium from the empirical viewpoint and later use thermodynamics to explain the empirical developments. Others prefer to develop the background of thermodynamics first and then apply it to chemical equilibrium. We have organized this chapter to allow either approach. After an introductory section on the general nature of chemical equilibrium, we introduce the equilibrium constant empirically in Section 14.2, and then give a thermodynamic description in Section 14.3. Similarly, we discuss the direction of change in chemical reactions empirically in Section 14.6 and give a thermodynamic treatment in Section 14.7. Readers who have studied thermodynamics before starting this chapter should read the sections in the order presented. Readers who have not yet studied thermodynamics should skip over Sections 14.3 and 14.7 and return to them after studying Chapters 12 and 13 on thermodynamics. We provide signposts for both sets of readers at the end of each section.

14.1 The Nature of Chemical Equilibrium

Approach to Equilibrium

Most chemical reactions are carried out by mixing the selected reactants in a vessel and adjusting T and P until the desired products appear. Once reaction conditions have been identified, the greatest concern is the yield of the reaction. How



(a) (b) (c) (d)

FIGURE 14.1 Chemical equilibrium in the cobalt chloride–HCl system. (a) The pink color is due to the hexaaqua complex ion $[Co(H_2O)_6]^{2+}$. (b) The blue color is due to the tetrachloro complex ion $[CoCl_4]^{2-}$. (c) Adding HCl to the pink solution in (a) converts some of the Co(II) to the tetrachloro complex. The lavender color is produced by the combination of pink hexaaqua species and blue tetrachloro species. (d) Adding water to the blue solution in (b) converts some of the Co(II) to the hexaaqua species. The combination of the two gives the lavender color. The same equilibrium state is reached by running the reaction from the left (c) and from the right (d).

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do we obtain the greatest amount of the desired product? How close to completion does the reaction proceed?

Let's start by observing a particular reaction that illustrates all the aspects of equilibrium we need to understand. We have selected the reactions of cobalt(II) ions in aqueous solutions in which chloride ion is also present because the progress and outcome of the reactions are directly visible. The cobalt(II) ions can form various different complex ions, depending on the amount of chloride present. For example, if $CoCl_2 \cdot 6H_2O$ is dissolved in pure water to the concentration 0.08 M, the resulting solution is pale pink in color due to the hexaaquacobalt(II) complex ion $[Co(H_2O)_6]^{2+}$ (Fig. 14.1a). If $CoCl_2 \cdot 6H_2O$ is dissolved in 10 M HCl to the concentration 0.08 M, the solution is deep blue due to the tetrachlorocobalt(II) complex ion $[CoCl_4]^{2-}$ (see Fig. 14.1b). Solutions containing a mixture of both Co(II) species are purple.

The hexaaqua complex can be converted into the tetrachloro complex by addition of chloride ion through the reaction

$$\left[Co(H_2O)_6\right]^{2+} + 4\ Cl^- \rightleftharpoons \left[CoCl_4\right]^{2-} + 6\ H_2O$$

If we add concentrated HCl (one of the reactants, on the left side of the equation) to the pink solution in Figure 14.1a until the Co(II) concentration is 0.044 M and the HCl concentration is 5.5 M, the result is a lavender-colored solution, a sample of which is shown in Figure 14.1c. Optical absorption spectroscopy measurements to be described in Chapter 20 confirm the presence of both Co(II) species in the solution in Figure 14.1c. Ninety-eight percent of the Co is found in

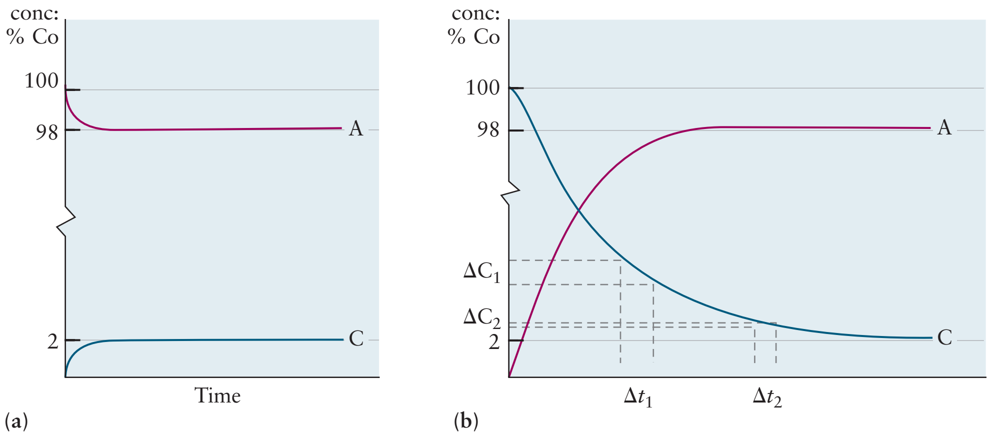

FIGURE 14.2 Sketch of the change with time of the concentrations of products and reactants in the spontaneous reactions illustrated in Figure 14.1. For ease of display, concentrations are expressed as percent of the total Co(II) present in each species. (a) Partial conversion of pink hexaaqua complex A into blue tetrachloro complex C. (b) Partial conversion of blue tetrachloro complex C into pink hexaaqua complex A. After changes in the slope of each species concentration become imperceptibly small, we say the reaction has arrived at chemical equilibrium.

the pink hexaaqua complex, and the remaining two percent is in the blue tetrachloro complex.[1] If the lavender solution is allowed to stand at constant temperature for several hours and the measurements repeated, the results are the same.

The reaction can also be carried out from "right to left" as written. If we add pure water (one of the products, on the right side of the equation) to the blue solution in Figure 14.1b until the cobalt concentration is 0.044 M and the HCl concentration is 5.5 M, the result is a lavender-colored solution, a sample of which is shown in Figure 14.1d. Just as we saw after running the reaction "left to right," optical absorption spectroscopy confirms that 98% of the Co(II) is present in the pink hexaaqua complex and 2% is present in the blue tetrachloro complex. Again, we find no further change in composition of the mixture after a long wait.

These data show that the reaction has not gone to completion but has apparently halted at an intermediate state containing products as well as unconsumed reactants. Moreover, the same final state can be achieved from either direction. This result is typical of most chemical reactions, even though it is not generally as readily apparent as here.

The questions raised in the first paragraph require quantitative investigations of the reaction mixture, which we carry out as follows. In the preceding reaction let A represent the pink hexaaqua complex, B the chloride ion, and C the blue tetrachloro complex. In the first experiment, we start the reaction by mixing initial concentrations of A and B, denoted as $[A]_0$ and $[B]_0$. As the reaction proceeds, we periodically sample the reaction mixture. For each sample, we measure the concentration of A, B, and C and plot concentration of each species versus time. The results of the first experiment are represented schematically in Figure 14.2a, which shows the consumption of A and the production of C. Similarly, we start the second experiment with the initial concentration $[C]_0$, and add water. The results are represented schematically in Figure 14.2b, which shows the consumption of C and the production of A.

As the reaction proceeds, we see that the concentration of each species changes progressively more slowly. This fact is indicated by the decreasing values of the slope $[m = \Delta(\text{conc.})/\Delta t]$ sketched on the concentration curves during progressively later time intervals. Eventually, the slopes become close enough to zero to show that the concentration of each species has become constant in time. When this condition has been achieved, we say the reaction is at *chemical equilibrium,* and

---

[1] It may appear surprising to find such imbalance in the concentration of the Co(II) species when the color intensities of the pink and lavender solutions in Figure 14.1a and Figure 14.1c appear quite similar. This difference is explained by the fact that the blue tetrachloro complex absorbs light much more efficiently than the pink hexaaqua complex.

the reaction mixture is at the *equilibrium composition*.[2] At later times, there is no further change in composition of the reaction mixture; the concentration of each of the species X = A, B, C remains at its equilibrium value denoted by $[X]_{eq}$.

Characteristics of the Equilibrium State

We can gain insight into the equilibrium state by comparing chemical reactions to the familiar phase equilibrium between liquid water and water vapor (see Section 10.4 and Figure 10.19). Let's represent the transfer of water molecules in this phase equilibrium as a chemical equation:

$$H_2O(\ell) \rightleftarrows H_2O(g)$$

The double arrows ($\rightleftarrows$) emphasize the dynamic nature of phase equilibrium: Liquid water evaporates to form water vapor and at the same time vapor condenses to give liquid. An analogous dynamic description applies to a chemical equilibrium, in which bonds are broken or formed as atoms move back and forth between reactant and product molecules. When the initial concentrations of the reactants are high, collisions between their molecules cause product molecules to form. Once the concentrations of the products have increased sufficiently, the reverse reaction (forming "reactants" from "products") begins to occur. As the equilibrium state is approached, the forward and backward rates of reaction become equal and there is no further net change in reactant or product concentrations. Just as the equilibrium between liquid water and water vapor is a dynamic process on the molecular scale, with evaporation and condensation taking place simultaneously, the chemical equilibrium between reactants and products also occurs through the continuous formation of molecules of product from reactant molecules and their reaction back into reactant molecules with equal rates. Chemical equilibrium is not a static condition, although macroscopic properties such as concentrations do stop changing when equilibrium is attained. Chemical equilibrium is the consequence of a dynamic balance between forward and backward reactions.

The experimental results shown in Figures 14.1 and 14.2 demonstrate that the same equilibrium state is reached whether one starts with the reactants or with the products. This fact can be used to test whether a system is truly in equilibrium or whether the reaction is just so slow that changes in concentration are unmeasurably small, even though the system is far from equilibrium. If the same state is reached from either reactants or products, that state is a true equilibrium state.

Equilibrium states have four fundamental characteristics:

1. They display no macroscopic evidence of change.
2. They are reached through spontaneous (in the sense of Chapter 13) processes.
3. They show a dynamic balance of forward and reverse processes.
4. They are the same regardless of direction of approach.

We frequently also encounter so-called *steady states* in which the macroscopic concentrations of species are not changing with time, even though the system is not at equilibrium. Steady states are maintained not by a dynamic balance between forward and reverse processes but rather by the competition between a process that supplies the species to the system and a process that removes the species from the system. Many chemical reactions occur in living systems in steady states and do not represent an equilibrium between reactants and products. You must be certain that a reaction is at equilibrium and not in steady state before applying the methods of this chapter to explain the relative concentrations of reactants and products.

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[2] You must exercise judgment in deciding when the slope is "sufficiently close to zero" and the concentrations are "effectively constant." There is no one instant at which equilibrium is achieved.

14.2 The Empirical Law of Mass Action

Let us examine again the approach to equilibrium, as represented in Figure 14.2 and the related discussion. Extensive studies of this type for broad classes of reactions represented generally as

$$a\mathrm{A} + b\mathrm{B} \rightleftarrows c\mathrm{C} + d\mathrm{D}$$

have demonstrated a most remarkable result. No matter what initial concentrations of reactants are selected at the beginning of the experiment, the value of the ratio

$$\frac{[\mathrm{C}]_{\mathrm{eq}}^{c}[\mathrm{D}]_{\mathrm{eq}}^{d}}{[\mathrm{A}]_{\mathrm{eq}}^{a}[\mathrm{B}]_{\mathrm{eq}}^{b}}$$

measured *at equilibrium* is always the same. Even if the experiment is started with an arbitrary initial mixture of reactants and products, the reaction will consume some species and produce others until it achieves this same value of this ratio at equilibrium. Consequently, this ratio is called the **empirical equilibrium constant** for the reaction and denoted as K_C. The results of these studies are summarized in the following equation called the **law of mass action,** first stated in approximate form in 1864 by two Norwegians, C. M. Guldberg (a mathematician) and his brother-in-law P. Waage (a chemist):

$$\frac{[\mathrm{C}]_{\mathrm{eq}}^{c}[\mathrm{D}]_{\mathrm{eq}}^{d}}{[\mathrm{A}]_{\mathrm{eq}}^{a}[\mathrm{B}]_{\mathrm{eq}}^{b}} = K_\mathrm{C} \qquad \textbf{[14.1a]}$$

The subscript C denotes that the reaction is carried out in solution and that the empirical equilibrium constant K_C is evaluated by directly measuring the concentration of each species in the equilibrium state of the reaction. In general, K_C has dimensions (concentration)$^{c+d-a-b}$; it will be dimensionless only for those reactions for which $a + b = c + d$.

Similar results have been obtained for reactions carried out in the gas phase, where the amount of each reactant and product in the reaction mixture is measured by its partial pressure P_X. For gas-phase reactions, the empirical law of mass action takes the form

$$\frac{(P_\mathrm{C})_{\mathrm{eq}}^{c}(P_\mathrm{D})_{\mathrm{eq}}^{d}}{(P_\mathrm{A})_{\mathrm{eq}}^{a}(P_\mathrm{B})_{\mathrm{eq}}^{b}} = K_\mathrm{P} \qquad \textbf{[14.1b]}$$

In general, K_P has dimensions (pressure)$^{c+d-a-b}$; it will be dimensionless only for those reactions for which $a + b = c + d$.

The significance of the empirical law of mass action is twofold. First, the numerical value of K_C or K_P is an inherent property of the chemical reaction itself and does not depend on the specific initial concentrations of reactants and products selected. Second, the magnitude of K_P or K_C gives direct information about the nature of the equilibrium state or position of the reaction. If the equilibrium constant is very large, then at equilibrium the concentration or partial pressures of products are large compared with those of the reactants. In this case, stoichiometry can be used to estimate the number of moles or the masses of product formed because the reaction is near completion. If the equilibrium constant is very small, the concentration or partial pressures of reactants are large compared with those for products, and the extent of reaction is very limited. If the equilibrium constant has a value close to 1, both reactants and products are present in significant proportions at equilibrium.

The law of mass action is the basis for equilibrium calculations, which pervade the science of chemistry. All follow the same general pattern: Suppose we know the numerical value of K_C or K_P for a reaction of interest. Furthermore, suppose we run an experiment by mixing selected initial concentrations of reactants. We can then use Equation 14.1 to calculate the concentration of the reaction products and reactants that will appear at equilibrium, without doing the laborious measurements described in Figure 14.2. In this and succeeding chapters in Unit 4, we demonstrate the methods of these calculations for reactions in the gas phase, for acid–base reactions involving ionic species in aqueous solutions, and for heterogeneous reactions occurring at the interface between different states of matter. In preparation for these calculations, we now show how to write the empirical law of mass action for these classes of reactions.

Law of Mass Action for Gas-Phase Reactions

Many reactions are conveniently carried out entirely in the gas phase. Molecules in the gas phase are highly mobile, and the collisions necessary for chemical reactions occur frequently. Two examples are the key steps in the production of hydrogen from the methane in natural gas. The first is the **reforming reaction:**

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$$

The second step is called the **shift reaction:**

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

This process is currently the main industrial method for the preparation of hydrogen. Its success relies critically on application of the equilibrium principles developed in this chapter.

To write the mass action law, a first glance at Equation 14.1b suggests we need only examine the balanced equation for the reaction and insert the partial pressure of each reactant and product into Equation 9.1b and raise it to a power equivalent to its stoichiometric coefficient in the balanced equation, to obtain a ratio with dimensions of $(\text{press.})^{c+d-a-b}$. A deeper study of equilibrium shows that instead of inserting just the partial pressure for each reactant or product, we must insert the value of the partial pressure *relative to* a specified reference pressure P_{ref}. The result is the following expression, denoted by K with no subscript

$$\frac{(P_C/P_{\text{ref}})^c(P_D/P_{\text{ref}})^d}{(P_A/P_{\text{ref}})^a(P_B/P_{\text{ref}})^b} = K$$

Note that K is dimensionless. Collecting the terms involving P_{ref} on the right side of the equation gives

$$\frac{P_C^c P_D^d}{P_A^a P_B^b} = K(P_{\text{ref}})^{(c+d-a-b)}$$

which must be equal to K_P. It is customary to choose P_{ref} as atmospheric pressure, which can be expressed as $P_{\text{ref}} = 1$ atm, $P_{\text{ref}} = 760$ torr, or $P_{\text{ref}} = 101{,}325$ Pa. If all pressures are expressed in atmospheres, then $P_{\text{ref}} = 1$ atm, and the right side shows that K_P has the same *numerical value* as the dimensionless quantity K, with P_{ref} factors serving only to make the equation dimensionally correct. If some other unit is chosen for pressures, the P_{ref} factors no longer have a numerical value of unity and must be inserted explicitly into the equilibrium expression.

The dimensionless quantity K is the **thermodynamic equilibrium constant,** which Section 14.3 shows can be calculated from tabulated data on the products and reactants, even if the empirical equilibrium constant defined in Equation 14.1b is not known. Therefore, K is the preferred tool for analyzing reaction equilibria in general. The informal argument by which we replaced K_P with K is made rigorous by the thermodynamic treatment of equilibrium in Section 14.3. Meantime, we can freely use the result in advance of formal justification.

The convention we follow in this book is to describe chemical equilibrium in terms of the thermodynamic equilibrium constant K, even when analyzing reactions empirically. Consequently, for gaseous reactions we will state values of K without dimensions, and we will express all pressures in atmospheres. The P_{ref} factors will not be explicitly included because their value is unity with these choices of pressure unit and reference pressure. Following this convention, we write the mass action law for a general reaction involving ideal gases as

$$\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} = K \qquad [14.2a]$$

with K dimensionless. The following example illustrates these practices.

EXAMPLE 14.1

Write equilibrium expressions for the following gas-phase chemical equilibria.

(a) $2\,\text{NOCl}(g) \rightleftharpoons 2\,\text{NO}(g) + \text{Cl}_2(g)$

(b) $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{CO}_2(g)$

SOLUTION

(a)

$$\frac{(P_{\text{NO}})^2(P_{\text{Cl}_2})}{(P_{\text{NOCl}_2})^2} = K$$

The powers of 2 come from the factors of 2 in the balanced equation.

(b)

$$\frac{(P_{\text{CO}_2})}{(P_{\text{CO}})(P_{\text{O}_2})^{1/2}} = K$$

Fractional powers appear in the equilibrium expression whenever they are present in the balanced equation.

Related Problems: 1, 2, 3, 4

Law of Mass Action for Reactions in Solution

A great many reactions are carried out in a convenient solvent for reactants and products. Dissolved reactants can be rapidly mixed, and the reaction process is easily handled. Water is a specially favored solvent because its polar structure allows a broad range of polar and ionic species to be dissolved. Water itself is partially ionized in solution, liberating H^+ and OH^- ions that can participate in reactions with the dissolved species. This leads to the important subject of acid–base equilibria in aqueous solutions (see Chapter 15), which is based on the equilibrium principles developed in this chapter. We limit the discussion in this subsection to cases in which the solvent does not participate in the reaction.

The procedure for reactions in solution follows the same informal discussion just given for gas-phase reactions. A deeper study of equilibrium shows that instead of inserting just the concentration for each reactant or product into Equation 14.1a, we must insert the value of concentration *relative to* a specified reference concentration c_{ref}. The result is the following expression, denoted by K with no subscript

$$\frac{([\text{C}]/c_{\text{ref}})^c([\text{D}]/c_{\text{ref}})^d}{([\text{A}]/c_{\text{ref}})^a([\text{B}]/c_{\text{ref}})^b} = K$$

The square bracket [X] represents the concentration of species X in units of mol L^{-1}. If all factors containing c_{ref} are collected on the right side and the reference state for each reactant and product is defined to be an ideal solution with a concentration $c_{\text{ref}} = 1$ M, then the same arguments used before for gas-phase reactions show that the dimensionless thermodynamic equilibrium constant K is numerically equal to K_C.

Just as with gaseous reactions, the convention we follow in this book is to describe solution equilibria in terms of the thermodynamic equilibrium constant K rather than the empirical K_C. Thus, we express solution concentrations in units of mol L^{-1} with the reference state as $c_{\text{ref}} = 1$ M, and we state values of K as dimensionless quantities. For these conditions the mass action law for solution reactions becomes

$$\boxed{\frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^c[\mathrm{B}]^b} = K} \qquad \textbf{[14.2b]}$$

The following example illustrates these practices.

EXAMPLE 14.2

Household laundry bleach is a solution of sodium hypochlorite (NaOCl) prepared by adding gaseous Cl_2 to a solution of sodium hydroxide:

$$\mathrm{Cl_2}(aq) \; + \; 2\,\mathrm{OH^-}(aq) \rightleftarrows \mathrm{ClO^-}(aq) + \mathrm{Cl^-}(aq) + \mathrm{H_2O}(\ell)$$

The active bleaching agent is the hypochlorite ion, which can decompose to chloride and chlorate ions in a side reaction that competes with bleaching:

$$3\,\mathrm{ClO^-}(aq) \rightleftarrows 2\,\mathrm{Cl^-}(aq) + \mathrm{ClO_3^-}(aq)$$

Write the equilibrium expression for the decomposition reaction.

SOLUTION

$$\frac{[\mathrm{Cl^-}]^2[\mathrm{ClO_3^-}]}{[\mathrm{ClO^-}]^3} = K$$

The exponents come from the coefficients in the balanced chemical equation.

Related Problems: 7, 8

Law of Mass Action for Reactions Involving Pure Substances and Multiple Phases

A variety of equilibria occur in heterogeneous systems that involve solids and liquids as well as gases and dissolved species. Molecular species cross the interfaces between phases in order to participate in reactions. A whole class of examples (Chapter 16) is based on the dissolution of slightly soluble salts, where the dissolved ions are in equilibrium with the pure solid. Another class includes the reaction of pure metals with acids to produce hydrogen gas:

$$\mathrm{Zn}(s) + 2\,\mathrm{H_3O^+}(aq) \rightleftarrows \mathrm{Zn^{2+}}(aq) + \mathrm{H_2}(g) + 2\,\mathrm{H_2O}(\ell)$$

Yet another example shows how iron sulfide residues from mining operations introduce iron and sulfur as pollutants in water streams:

$$4\,\mathrm{FeS_2}(s) + 15\,\mathrm{O_2}(g) + 6\,\mathrm{H_2O}(\ell) \rightleftarrows 4\,\mathrm{Fe(OH)^{2+}}(aq) + 8\,\mathrm{HSO_4^-}(aq)$$

Reactions in aqueous solution sometimes involve water as a direct participant. In addition to familiar aqueous acid–base chemistry, many organic reactions fall into this class. One example is the hydrolysis of ethyl acetate to produce acetic acid and ethanol:

$$CH_3COOC_2H_5(aq) + H_2O(\ell) \rightleftarrows CH_3COOH(aq) + C_2H_5OH(aq)$$

Several examples illustrate the procedures for writing the mass action law for heterogeneous reactions and for reactions involving pure solids or liquids.

1. Recall the phase equilibrium between liquid water and water vapor from Section 5.4:

$$H_2O(\ell) \rightleftarrows H_2O(g) \qquad P_{H_2O} = K$$

Experiments show that as long as *some* liquid water is in the container, the pressure of water vapor at 25°C is 0.03126 atm. The position of this equilibrium is not affected by the amount of liquid water present, and therefore liquid water should not appear in the mass action law. Recall that for a gas or solute, a ratio of pressures or concentrations appears in the law of mass action. This ratio is equal to 1 when the gas or solute is in its reference state (1 atm or 1 M). For a pure liquid appearing in an equilibrium chemical equation, the convention is to take that pure liquid as the reference state, so the liquid water contributes only a factor of 1 to the equilibrium expression and can thus be entirely omitted. We postpone justification of this rule to Section 14.3.

2. An analogous situation occurs in the equilibrium between solid iodine and iodine dissolved in aqueous solution:

$$I_2(s) \rightleftarrows I_2(aq) \qquad [I_2] = K$$

Experiment shows that the position of the equilibrium (given by the concentration of I_2 dissolved at a given temperature) is independent of the amount of solid present, as long as there is some. The pure solid iodine does not appear in the mass action law, for the same reason pure liquid water did not appear in the preceding case.

3. Another example involves a chemical reaction, the decomposition of calcium carbonate:

$$CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g) \qquad P_{CO_2} = K$$

If calcium carbonate is heated, it decomposes into calcium oxide (lime) and carbon dioxide; the reverse reaction is favored at sufficiently high pressures of carbon dioxide. The equilibrium can be studied experimentally, and it is found that at any given temperature the pressure of $CO_2(g)$ is constant, independent of the amounts of $CaCO_3(s)$ and $CaO(s)$, as long as some of each is present (Fig. 14.3). The two pure solids do not appear in the mass action law, which reduces to the partial pressure of CO_2.

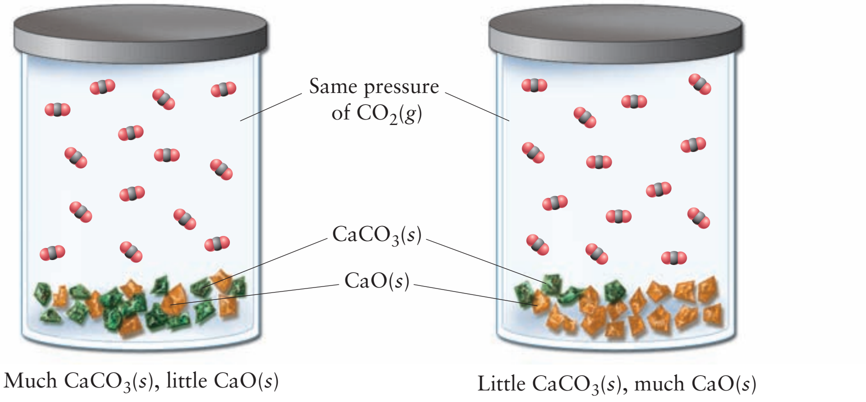

FIGURE 14.3 As long as both $CaO(s)$ and $CaCO_3(s)$ are present at equilibrium in a closed container, the partial pressure of $CO_2(g)$ at a fixed temperature does not depend on the amounts of the two solids present.

The general procedure for writing the mass action law for these more complex reactions is the following:

1. Gases enter the equilibrium expression as partial pressures, measured in atmospheres.
2. Dissolved species enter as concentrations, in moles per liter.
3. Pure solids and pure liquids do not appear in equilibrium expressions; neither does a solvent taking part in a chemical reaction, provided the solution is dilute.
4. Partial pressures and concentrations of products appear in the numerator, and those of reactants in the denominator; each is raised to a power equal to its coefficient in the balanced chemical equation for the reaction.

This procedure gives the dimensionless thermodynamic equilibrium constant K because each species has entered the equilibrium expression relative to its standard reference state. This procedure will be justified by the thermodynamic treatment of equilibrium in Section 14.3, but it can be used with confidence in advance of that justification.

The following example illustrates these practices.

EXAMPLE 14.3

Hypochlorous acid (HOCl) is produced by bubbling chlorine through an agitated suspension of mercury(II) oxide in water. The chemical equation for this process is

$$2\,\mathrm{Cl_2}(g) + 2\,\mathrm{HgO}(s) + \mathrm{H_2O}(\ell) \rightleftharpoons \mathrm{HgO{\cdot}HgCl_2}(s) + 2\,\mathrm{HOCl}(aq)$$

Write the equilibrium expression for this reaction.

SOLUTION

$$\frac{[\mathrm{HOCl}]^2}{P_{\mathrm{Cl_2}}^2} = K$$

The HgO and $HgO{\cdot}HgCl_2$ do not appear because they are solids, and water does not appear because it is the solvent. Chlorine, as a gas, enters as its partial pressure in atmospheres. The HOCl appears as its concentration, in moles per liter. Both the concentration of HOCl and the partial pressure of Cl_2 are raised to the second power because their coefficients in the balanced chemical equation are 2.

Related Problems: 9, 10, 11, 12

The preceding discussion has specified the procedures for setting up the mass action law for broad classes of chemical reactions. The resulting expressions are ready to be used in equilibrium calculations.

Despite their success in giving the correct expressions for the mass action law, the empirical procedures leave unanswered numerous fundamental questions about chemical equilibrium. Why should the law of mass action exist in the first place, and why should it take the particular mathematical form shown here? Why should the equilibrium constant take a unique value for each individual chemical reaction? What factors determine that value? Why does the value of the equilibrium constant change slightly when studied over broad ranges of concentration? Why should the equilibrium constant depend on temperature? Is there a quantitative explanation for the temperature dependence?

All these questions are answered by the thermodynamic description of the equilibrium constant, provided in the next section. Readers who have already studied thermodynamics should continue to Section 14.3.

Readers who have not yet studied thermodynamics should go to Sections 14.4 and 14.5, which give detailed analysis of equilibrium calculations based on the mass action law procedures just described. Sections 14.4 and 14.5 do not require background in thermodynamics.

14.3 Thermodynamic Description of the Equilibrium State

In this section we use thermodynamics to demonstrate why the mass action law takes its special mathematical form and why the thermodynamic equilibrium constant K is a dimensionless quantity. This demonstration justifies the procedures we presented in Section 14.2 for writing down the mass action law by inspection for any chemical reaction. In addition, thermodynamics gives a method for calculating the value of K from tabulated properties of the reactants and products. Consequently, the value of K can be obtained for a reaction, even if the empirical equilibrium constant K_C or K_P has not been measured. Thermodynamics also explains how K changes when the reaction is run under different experimental conditions. With this information, we can manipulate reaction conditions to obtain maximum yield from the reaction.

Thermodynamics views a chemical reaction as a process in which atoms "flow" from reactants to products. If the reaction is spontaneous and is carried out at constant T and P, thermodynamics requires that $\Delta G < 0$ for the process (see Section 13.7). Consequently, G always *decreases* during a spontaneous chemical reaction. When a chemical reaction has reached equilibrium, $\Delta G = 0$; that is, there is no further tendency for the reaction to occur in either the forward or the reverse direction. We will use the condition $\Delta G = 0$ in the following three subsections to develop the mass action law and the thermodynamic equilibrium constant for gaseous, solution, and heterogeneous reactions.

Reactions among Ideal Gases

Before we develop the mass action law, it is necessary to investigate how the Gibbs free energy changes with pressure at constant temperature, because in chemical equilibria, the partial pressures of gases can differ from 1 atm.

DEPENDENCE OF GIBBS FREE ENERGY OF A GAS ON PRESSURE If the pressure of an ideal gas is changed from P_1 to P_2 with the temperature held constant, the free energy change is

$$\Delta G = \Delta(H - TS) = \Delta H - T\Delta S = -T\Delta S$$

The last equality is true because $\Delta H = 0$ when the pressure of an ideal gas is changed at constant temperature. The entropy change for an ideal gas in an isothermal process was calculated in Section 13.5:

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right) = nR \ln\left(\frac{P_1}{P_2}\right) = -nR \ln\left(\frac{P_2}{P_1}\right)$$

so

$$\Delta G = nRT \ln\left(\frac{P_2}{P_1}\right) \qquad [14.3a]$$

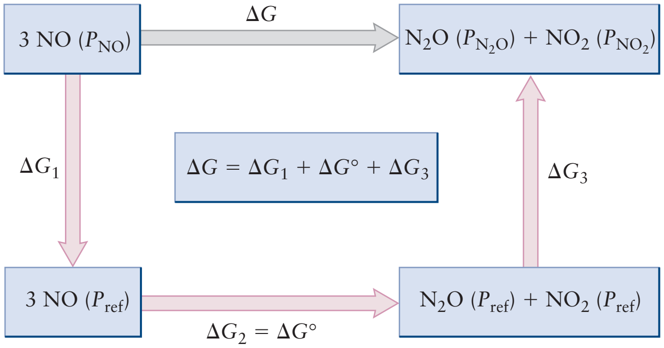

FIGURE 14.4 A three-step process (red arrows) to calculate ΔG of a reaction (blue arrow) for which reactants and products are not in their standard states of 1 atm.

Let us choose the value of P_1 to be 1 atm, which has already been defined as the standard state of gaseous substances for measurements both of enthalpy of formation (see Section 12.5) and Gibbs free energy of formation (see Section 13.7). Then, Equation 14.3a relates the Gibbs free energy of the gas at any pressure P_2 to its value at 1 atm. This result can be expressed compactly as follows. If we call 1 atm the *reference state* for the gas, then the change in Gibbs free energy in taking the gas from the reference state to any pressure P is given by

$$\Delta G = nRT \ln\left(\frac{P}{P_{ref}}\right) = nRT \ln P \qquad [14.3b]$$

Equation 14.3b is a shorthand version that can be used only when the pressure P is expressed in atm. The presence of P_{ref} in the denominator makes the argument of the natural logarithm function dimensionless. Choosing $P_{ref} = 1$ atm gives P_{ref} the numerical value 1, which for convenience we do not write explicitly. Nonetheless, you should always remember this (invisible) P_{ref} is required to make the equation dimensionally correct when the general pressure P in the equation is expressed in atm. If some unit of pressure other than atm is selected, P_{ref} no longer has value 1 and the P_{ref} selected must be carried explicitly in the equations.

THE EQUILIBRIUM EXPRESSION FOR REACTIONS IN THE GAS PHASE

Consider now a mixture of gases that react chemically, such as the NO, N_2O, and NO_2 given in Example 13.10:

$$3\,NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$$

If all of the partial pressures are 1 atm, then ΔG for this reaction is just $\Delta G°$ at 25°C. If the pressures differ from 1 atm, ΔG must be calculated from a three-step process (Fig. 14.4). In step 1 the partial pressure of the reactant (in this case, 3 mol of NO) is changed from its initial value, P_{NO}, to the reference pressure $P_{ref} = 1$ atm:

$$\Delta G_1 = 3RT \ln\left(\frac{P_{ref}}{P_{NO}}\right) = RT \ln\left(\frac{P_{ref}}{P_{NO}}\right)^3$$

In step 2 the reaction is carried out with all reactants and products at partial pressures of $P_{ref} = 1$ atm:

$$\Delta G_2 = \Delta G°$$

In step 3 the partial pressures of the products (in this case, 1 mol of N_2O and 1 mol of NO_2) are changed from $P_{ref} = 1$ atm to P_{N_2O} and P_{NO_2}:

$$\Delta G_3 = RT \ln\left(\frac{P_{N_2O}}{P_{ref}}\right) + RT \ln\left(\frac{P_{NO_2}}{P_{ref}}\right) = RT \ln\left[\left(\frac{P_{N_2O}}{P_{ref}}\right)\left(\frac{P_{NO_2}}{P_{ref}}\right)\right]$$

The overall Gibbs free energy change ΔG for the reaction is the sum of the free energy changes for the three steps in the path:

$$\begin{aligned}\Delta G &= \Delta G_1 + \Delta G_2 + \Delta G_3 \\ &= \Delta G° + RT \ln \left[\frac{(P_{N_2O}/P_{ref})(P_{NO_2}/P_{ref})}{(P_{NO}/P_{ref})^3}\right]\end{aligned}$$

When a chemical reaction has reached equilibrium, $\Delta G = 0$. Under these conditions the preceding equation becomes

$$-\Delta G° = RT \ln \left[\frac{(P_{N_2O}/P_{ref})(P_{NO_2}/P_{ref})}{(P_{NO}/P_{ref})^3}\right]$$

Because $\Delta G°$ depends only on temperature, the quantity $\Delta G°/RT$ must be a constant at each value of T. Therefore, in the last equation, the ratio of partial pressures inside the natural logarithm function must also be constant *at equilibrium* at each value of T. Consequently, this ratio of partial pressures is denoted by $K(T)$ and is called the *thermodynamic equilibrium constant* for the reaction. Finally, we have

$$-\Delta G° = RT \ln K(T) \qquad \textbf{[14.4]}$$

For the general reaction

$$aA + bB \longrightarrow cC + dD$$

the result, obtained in the same way, is

$$-\Delta G° = RT \ln \left[\frac{(P_C/P_{ref})^c(P_D/P_{ref})^d}{(P_A/P_{ref})^a(P_B/P_{ref})^b}\right] = RT \ln K(T) \qquad \text{(at equilibrium)}$$

The expression for the thermodynamic equilibrium constant for reactions involving ideal gases,

$$\left[\frac{(P_C/P_{ref})^c(P_D/P_{ref})^d}{(P_A/P_{ref})^a(P_B/P_{ref})^b}\right] = K$$

has the same form as the empirical law of mass action with K_P for gaseous reactions introduced in Section 14.2. The thermodynamic expression provides deeper understanding of that empirical result in three important ways. First, the law of mass action, previously introduced on purely empirical grounds to describe chemical equilibrium, is seen to be a consequence of the reaction system being in thermodynamic equilibrium. Second, the thermodynamic equilibrium constant can be calculated from $\Delta G°$ (that is, from $\Delta H°$ and $\Delta S°$), so the *extent* of any equilibrium chemical reaction can be deduced from calorimetric data alone. Third, unlike K_P, the thermodynamic equilibrium constant K is always a dimensionless quantity because the pressure of a reactant or product always appears as a ratio to the reference pressure P_{ref}. The algebraic rearrangements leading to Equation 14.2a have already shown that K is numerically equal to K_P if we express all partial pressures in units of atm and select the reference state to be $P_{ref} = 1$ atm. Other choices of pressure units or reference states require the P_{ref} factors to be carried explicitly.

The convention we follow in this book, already stated in Section 14.2, is to describe chemical equilibrium in terms of the thermodynamic equilibrium constant K and to emphasize the fact that K can be obtained easily from tabulated thermodynamic data. Following this convention, the mass action law for a general reaction involving ideal gases is written as

$$\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} = K$$

with K dimensionless. The value of K can be calculated from Equation 14.4 using tables of data in Appendix D. The following example illustrates these practices.

EXAMPLE 14.4

The $\Delta G°$ of the chemical reaction

$$3\ NO(g) \longrightarrow N_2O(g) + NO_2(g)$$

was calculated in Example 13.10. Now calculate the equilibrium constant of this reaction at 25°C.

SOLUTION

The standard free energy change for the conversion of 3 mol of NO to 1 mol of N_2O and 1 mol of NO_2 was found to be -104.18 kJ. To keep the units of the calculation correct, the $\Delta G°$ is rewritten as $-104.18\ \text{kJ mol}^{-1}$, where "per mole" signifies "per mole of the reaction as it is written," that is, per 3 mol of NO, 1 mol of N_2O, and 1 mol of NO_2, the number of moles in the balanced equation. Substitution gives

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-(-104{,}180\ \text{J mol}^{-1})}{(8.315\ \text{J K}^{-1}\text{mol}^{-1})(298.15\ \text{K})} = 42.03$$

$$K = e^{42.03} = 1.8 \times 10^{18}$$

Related Problems: 13, 14

The conversion of $NO(g)$ to $N_2O(g)$ plus $NO_2(g)$ is spontaneous under standard conditions. The forward reaction under these conditions is scarcely observed because its rate is so slow. Nonetheless, its equilibrium constant can be calculated! Such calculations often have enormous impact in evaluating proposed solutions to practical problems. For example, the calculation shows that this reaction could be used to reduce the amount of NO in cooled exhaust gases from automobiles. The fundamental reaction tendency is there, but successful application requires finding a route to increasing the reaction rate at standard conditions. Had the equilibrium constant calculated from thermodynamics been small, this proposed application would be doomed at the outset and investment in it would not be justified.

Reactions in Ideal Solutions

The thermodynamic description of reactions in solution parallels the discussion just completed for ideal gas reactions. Although the result is not derived here, the Gibbs free energy change for n mol of a solute, as an ideal (dilute) solution changes in concentration from c_1 to c_2 mol L^{-1}, is

$$\Delta G = nRT \ln\left(\frac{c_2}{c_1}\right) \qquad \textbf{[14.5a]}$$

If the reference state for the solute is defined to be an ideal solution with a concentration $c_{\text{ref}} = 1$ M, the change in Gibbs free energy for taking the solution from the reference state to the concentration c is given by

$$\Delta G = nRT \ln\left(\frac{c}{c_{\text{ref}}}\right) = nRT \ln c \qquad \textbf{[14.5b]}$$

The same arguments used for gas-phase reactions show that the overall change in Gibbs free energy for a reaction in solution is

$$\Delta G = \Delta G° + RT \ln\left[\frac{([C]/c_{\text{ref}})^c([D]/c_{\text{ref}})^d}{([A]/c_{\text{ref}})^a([B]/c_{\text{ref}})^b}\right]$$

where the square bracket [X] represents the concentration of species X in units of mol L^{-1}. When the reaction arrives at equilibrium, $\Delta G = 0$, and the equilibrium constant is given by

$$-\Delta G° = RT \ln K \qquad \textbf{[14.6]}$$

for reactions involving dissolved species.

Following the convention already stated for gaseous reactions, in this book we describe solution equilibria in terms of the thermodynamic equilibrium constant K rather than the empirical K_C introduced in Section 14.2. Thus, we give solution concentrations in units of mol L^{-1} with the reference state as $c_{ref} = 1$ M, and state values of K as dimensionless quantities. For this convention, the mass action law for solution reactions becomes

$$\frac{[C]^c[D]^d}{[A]^c[B]^b} = K$$

and is numerically equivalent to K_C. When working with this expression, you must keep in mind the role of the (invisible) c_{ref} factors in making the equation dimensionally correct. This expression is the foundation for the discussions of acid–base equilibria in aqueous solutions in the next chapter.

Solution-phase equilibrium constants can be calculated from tables of standard free energies for solutes in aqueous solution at 25°C (see Appendix D). The procedure is demonstrated by the following example.

EXAMPLE 14.5

Calculate $\Delta G°$ and the equilibrium constant at 25°C for the chemical reaction

$$3\ \mathrm{ClO}^-(aq) \rightleftarrows 2\ \mathrm{Cl}^-(aq) + \mathrm{ClO}_3^-(aq)$$

whose equilibrium expression we developed in Example 14.2

SOLUTION

We calculate the change in standard Gibbs free energy using the ΔG_f° values for these aqueous ions in their standard states tabulated in Appendix D:

$$\begin{aligned}\Delta G° &= 2\ \Delta G_f^\circ(\mathrm{Cl}^-(aq)) + \Delta G_f^\circ(\mathrm{ClO}_3^-(aq)) - 3\ \Delta G_f^\circ(\mathrm{ClO}^-(aq))\\ &= (2\text{ mol})(-131.23\text{ kJ mol}^{-1}) + (1\text{ mol})(-7.95\text{ kJ mol}^{-1}) -\\ &\quad (3\text{ mol})(-36.8\text{ kJ mol}^{-1})\\ &= -160.01\text{ kJ}\end{aligned}$$

As in Example 14.4, we calculate K by inserting the value for $\Delta G°$ into the equation

$$\ln K = \frac{-\Delta G°}{RT} = \frac{-(-160{,}010\text{ J mol}^{-1})}{(8.315\text{ J K}^{-1}\text{mol}^{-1})(298.15\text{ K})} = 64.54$$

$$K = e^{64.54} = 1.1 \times 10^{28}$$

The decomposition of hypochlorite ion in bleach is thus a spontaneous process, with a very large equilibrium constant at 25°C. But, this reaction is very slow at room temperature, so the laundry bleach solution remains stable. If the temperature is raised to about 75°C, the reaction occurs rapidly and the bleach solution decomposes.

Reactions Involving Pure Solids and Liquids and Multiple Phases: The Concept of Activity

The mass action law for homogeneous reactions in ideal gases and ideal solutions was written in Section 14.2 by straightforward inspection of the balanced equation for the reaction under study. If one or more of the reactants or products was a solid or liquid in its pure state, the procedure was less obvious, because "concentration" has no meaning for a pure species. This apparent difficulty is resolved by the concept of **activity,** which is a convenient means for comparing the properties of a substance in a general thermodynamic state with its properties in a specially selected reference state. A full treatment of equilibrium in terms of activity requires thermodynamic results beyond the scope of this book. Here we sketch the essential ideas leading to the more general form of the mass action law and merely state the range of validity of the idealized expressions presented.

The activity concept arises from the dependence of the Gibbs free energy on the pressure of a pure substance or on the composition of a solution, regardless of the phase of the system. The discussion just before Equation 14.3 shows that the change in Gibbs free energy when a gas is taken from a reference state P_{ref} to any pressure P is given by

$$\Delta G = nRT \ln\left(\frac{P}{P_{\text{ref}}}\right) = nRT \ln P$$

The last form is used only when pressure P is expressed in atmospheres and $P_{\text{ref}} = 1$ atm. A similar equation can be developed for more complex systems—and keep the same simple mathematical form—if we *define* the activity by the equation

$$\Delta G = nRT \ln a \qquad [14.7]$$

Of course if a system is already in its reference state, then $\Delta G = 0$ and the activity in this state is 1. The change in Gibbs free energy in taking a system from the reference state to any general thermodynamic state determines the activity a in the general state.

The activity is connected to pressure or to concentration by the **activity coefficient.** The *activity coefficient* γ_{i} of a nonideal gaseous species at pressure P_{i} is defined by the equation

$$a_{\text{i}} = \frac{\gamma_{\text{i}} P_{\text{i}}}{P_{\text{ref}}} \qquad [14.8a]$$

The reference state is chosen to be an ideal gas at one atmosphere. Comparing Equations 14.7 and 14.8a with Equation 14.3 shows that γ_{i} takes the value 1 for ideal gases. The activity of an ideal gas is the ratio of its pressure to the selected reference pressure. If pressures are given in units of atmospheres, then the activity of an ideal gas is numerically equal to its pressure. Similarly, the activity coefficient γ_{i} for solute i in a solution at concentration c_{i} is defined by the equation

$$a_{\text{i}} = \frac{\gamma_{\text{i}} c_i}{c_{\text{ref}}} \qquad [14.8b]$$

The activity coefficient γ_{i} equals 1 in the reference state, selected as an ideal solution with convenient concentration. For solute species in the dilute solutions considered in this book, concentration is most conveniently expressed in molarity, and the reference state is selected to be an ideal solution at concentration $c_{\text{ref}} = 1$ M.

The reference states for pure solids and liquids are chosen to be those forms stable at 1 atm, just as in the definition of standard states for enthalpy of formation (see Chapter 12) and Gibbs free energy of formation (see Chapter 13). Pure substances in their reference states are assigned activity of value 1.

Once reference states have been defined, the activity coefficients γ_{i} can be determined from experimental P-V-T and calorimetric data by procedures that are not described in this book. Then, Equation 14.7 can be written explicitly in terms of pressure, temperature, and concentrations when needed for specific calculations. In its present version, Equation 14.7 is especially well suited for general discussions, because it summarizes much complicated information about nonideal systems in a simple and compact form.

Starting from Equation 14.7, arguments similar to those preceding Equation 14.4 lead to the following expression for the thermodynamic equilibrium constant K regardless of the phase of each product or reactant:

$$\frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} = K \qquad [14.9]$$

Substituting the appropriate ideal expression for the activity of gaseous or dissolved species from Equation 14.8a or 14.8b leads to the forms of the mass action law and the equilibrium constant K already derived earlier in Section 14.3 for reactions in ideal gases or in ideal solutions. We write the mass action law for reactions involving pure solids and liquids and multiple phases by substituting unity for the activity of pure liquids or solids and the appropriate ideal expression for the activity of each gaseous or dissolved species into Equation 14.9. Once a proper reference state and concentration units have been identified for *each* reactant and product, we use tabulated free energies based on these reference states to calculate the equilibrium constant.

The following example illustrates the essential points.

EXAMPLE 14.6

The compound urea, important in biochemistry, can be prepared in aqueous solution by the following reaction:

$$CO_2(g) + 2\ NH_3(g) \rightleftharpoons CO(NH_2)_2(aq) + H_2O(\ell)$$

(a) Write the mass action law for this reaction. **(b)** Calculate $\Delta G°$ for this reaction at 25°C. **(c)** Calculate K for this reaction at 25°C.

SOLUTION

(a) In terms of activities for each species, the equilibrium expression is

$$\frac{a_{\text{urea}} \cdot a_{H_2O}}{a_{CO_2} \cdot a_{NH_3}^2} = K$$

Choose the reference state for the gases to be $P_{\text{ref}} = 1$ atm, for the urea to be $c_{\text{ref}} = 1$ M, and for water to be the pure liquid with unit activity. Then at low pressures and concentrations, the limiting idealized mass action law is

$$\frac{[\text{urea}]}{P_{CO_2} \cdot P_{NH_3}^2} = K$$

with [urea] in units of mol L^{-1} and the partial pressures in atm. The (invisible) P_{ref} and c_{ref} factors must always be kept in mind, because they make K dimensionless in this expression. This expression can be extended to higher pressures and concentrations, where nonideality becomes important, by inserting the appropriate activity coefficients.

(b) The procedure is the same as in Examples 14.4 and 14.5. The $\Delta G_f°$ values for gaseous CO_2 and NH_3 and liquid H_2O with the reference states just specified are obtained directly from Appendix D. Because the data for urea in Appendix D are based on a *solid* reference state, we consult an alternate source[3] to obtain $\Delta G_f°(\text{urea}(aq)) = -203.84$ kJ mol^{-1} with the reference state an ideal solution with $c = 1$ M. From these data obtain

$$\Delta G° = -203.84 - 237.18 + 394.36 + 2\,(16.48) = -13.70 \text{ kJ mol}^{-1}$$

(c) Following the procedure in Example 14.5 we find $K = 251.1$.

This example illustrates a very important point: Before using $\Delta G_f°$ values to estimate equilibrium constants, *be certain* you know the reference state for the tabulated values.

Related Problems: 15, 16

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[3] Thermodynamic data for many biological molecules in solution are given in F. H. Carpenter, *J. Am. Chem. Soc.*, *82*, 1120 (1960).

The procedure for writing the mass action law for this class of reactions given at the end of Section 14.2 was based on informal discussion and included one rote rule. The procedure is now justified by the activity concept.

Equilibrium expressions written in this way are accurate to about 5% when the pressures of gases do not exceed several atmospheres and the concentrations of solutes do not exceed 0.1 M. These cases cover all the applications discussed in this book, so we do not need correction factors. For concentrated ionic solutions, the corrections can become very large. In accurate studies of solution equilibria, especially in biochemical applications, activities must be used in place of partial pressures or concentrations. You should consult more advanced books when you need these techniques.

14.4 The Law of Mass Action for Related and Simultaneous Equilibria

Each time we write the mass action law, it is based on a specific balanced chemical equation in which the reaction is carried out as written "left to right." Chemical reactions can be carried out in various alternative ways, including "in reverse" and in concert with other reactions. These variations lead to relationships among equilibrium expressions, which are best illustrated in a series of examples.

Relationships among Equilibrium Expressions

(1) Suppose a reaction is written in two opposing directions:

$$2\ H_2(g) + O_2(g) \rightleftharpoons 2\ H_2O(g) \qquad \frac{P_{H_2O}^2}{P_{H_2}^2 P_{O_2}} = K_1$$

$$2\ H_2O(g) \rightleftharpoons 2\ H_2(g) + O_2(g) \qquad \frac{P_{H_2}^2 P_{O_2}}{P_{H_2O}^2} = K_2$$

In the first reaction, hydrogen and oxygen combine to form water vapor, whereas in the second, water vapor dissociates into hydrogen and oxygen. The equilibrium constants K_1 and K_2 are clearly the inverse of each other, so their product $K_1K_2 = 1$. This is true quite generally: The equilibrium constant for a reverse reaction is the reciprocal of the equilibrium constant for the corresponding forward reaction.

(2) What happens if a balanced chemical equation is multiplied by a constant? In the preceding example, multiplying the first equation by $\frac{1}{2}$ gives

$$H_2(g) + \tfrac{1}{2}\, O_2(g) \rightleftharpoons H_2O(g)$$

This is a perfectly satisfactory way to write the equation for the chemical reaction; it says that 1 mol of hydrogen reacts with $\frac{1}{2}$ mol of oxygen to yield 1 mol of water vapor. The corresponding equilibrium expression is

$$\frac{P_{H_2O}}{P_{H_2} P_{O_2}^{1/2}} = K_3$$

Comparison with the expression for K_1 shows that

$$K_3 = K_1^{1/2}$$

When a balanced chemical equation is multiplied by a constant factor, the corresponding equilibrium constant is raised to a power equal to that factor.

(3) A further variation is to add two equations to give a third. In this case the equilibrium constant for the third equation is the product of the equilibrium constants for the first two. For example, at 25°C,

$$2\ \mathrm{BrCl}(g) \rightleftharpoons \mathrm{Cl_2}(g) + \mathrm{Br_2}(g) \qquad \frac{P_{\mathrm{Cl_2}}P_{\mathrm{Br_2}}}{P_{\mathrm{BrCl}}^2} = K_1 = 0.45$$

$$\mathrm{Br_2}(g) + \mathrm{I_2}(g) \rightleftharpoons 2\ \mathrm{IBr}(g) \qquad \frac{P_{\mathrm{IBr}}^2}{P_{\mathrm{Br_2}}P_{\mathrm{I_2}}} = K_2 = 0.051$$

Adding the two chemical equations gives

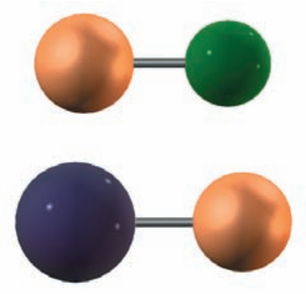
$$2\ \mathrm{BrCl}(g) + \mathrm{Br_2}(g) + \mathrm{I_2}(g) \rightleftharpoons 2\ \mathrm{IBr}(g) + \mathrm{Cl_2}(g) + \mathrm{Br_2}(\mathrm{g})$$

Removing $\mathrm{Br_2}(g)$ from both sides leaves

$$2\ \mathrm{BrCl}(g) + \mathrm{I_2}(g) \rightleftharpoons 2\ \mathrm{IBr}(g) + \mathrm{Cl_2}(g) \qquad \frac{P_{\mathrm{IBr}}^2P_{\mathrm{Cl_2}}}{P_{\mathrm{BrCl}}^2P_{\mathrm{I_2}}} = K_3$$

and, by inspection, $K_3 = K_1K_2 = (0.45)(0.051) = 0.023$.

(4) If a second equation is *subtracted* from the first, the resulting equilibrium constant is that of the first *divided* by that of the second (subtracting a reaction is the same as adding the reverse reaction). The operations of addition and subtraction applied to chemical equations transform into multiplication and division of the equilibrium expressions and equilibrium constants.



Bromine chloride, BrCl (top), and iodine bromide, IBr (bottom), are two examples of *interhalogens,* combinations of two or more halogen elements.

EXAMPLE 14.7

The concentrations of the oxides of nitrogen are monitored in air-pollution reports. At 25°C, the equilibrium constant for the reaction

$$\mathrm{NO}(g) + \tfrac{1}{2}\ \mathrm{O_2}(g) \rightleftharpoons \mathrm{NO_2}(g)$$

is

$$\frac{P_{\mathrm{NO_2}}}{P_{\mathrm{NO}}P_{\mathrm{O_2}}^{1/2}} = K_1 = 1.3 \times 10^6$$

and that for

$$\tfrac{1}{2}\ \mathrm{N_2}(g) + \tfrac{1}{2}\ \mathrm{O_2}(g) \rightleftharpoons \mathrm{NO}(g)$$

is

$$\frac{P_{\mathrm{NO_2}}}{P_{\mathrm{N_2}}^{1/2}P_{\mathrm{O_2}}^{1/2}} = K_2 = 6.5 \times 10^{-16}$$

Find the equilibrium constant K_3 for the reaction

$$\mathrm{N_2}(g) + 2\ \mathrm{O_2}(g) \rightleftharpoons 2\ \mathrm{NO_2}(g)$$

SOLUTION

Adding the chemical equations for the first two reactions gives

$$\tfrac{1}{2}\ \mathrm{N_2}(g) + \mathrm{O_2}(g) \rightleftharpoons \mathrm{NO_2}(g)$$

The equilibrium constant for this reaction, K_3', is just the product of K_1 and K_2, or K_1K_2. The constant sought, K_3, is defined by a chemical equation that is twice this, so K_3' must be raised to the power 2 (that is, squared) to give K_3:

$$K_3 = (K_3')^2 = (K_1K_2)^2 = 7.1 \times 10^{-19}$$

Related Problems: 17, 18, 19, 20

Consecutive Equilibria

Many real-world applications of chemistry and biochemistry involve fairly complex sets of reactions occurring in sequence and/or in parallel. Each of these individual reactions is governed by its own equilibrium constant. How do we describe the overall progress of the entire coupled set of reactions? We write all the involved equilibrium expressions and treat them as a set of *simultaneous algebraic equations,* because the concentrations of various chemical species appear in several expressions in the set. Examination of relative values of equilibrium constants shows that some reactions dominate the overall coupled set of reactions, and this chemical insight enables mathematical simplifications in the simultaneous equations. We study coupled equilibria in considerable detail in Chapter 15 on acid–base equilibrium. Here, we provide a brief introduction to this topic in the context of an important biochemical reaction.

Hemoglobin and Oxygen Transport

The cells of the human body need oxygen for life, and the bloodstream satisfies this need by transporting oxygen from the lungs. Whole blood can carry as much as 0.01 mol of O_2 per liter because the compound hemoglobin (Hb) in the red blood cells binds O_2 chemically. In contrast, blood plasma, which contains no hemoglobin, dissolves only about 0.0001 mol of O_2 per liter, a value that is close to the solubility of O_2 in ordinary water at room conditions. As highly oxygenated blood from the lungs passes through the capillaries, the binding of oxygen to hemoglobin loosens and the freed O_2 is taken up by a different oxygen-binding compound, called myoglobin (Mb), which is found in nearby cells. Myoglobin then carries the oxygen to the cells, where it is converted to carbon dioxide.

Why is oxygen held so tightly by hemoglobin in the lungs, then released so readily to myoglobin in the capillaries? The answer starts with a comparison of the heterogeneous equilibria by which hemoglobin and myoglobin bind oxygen. Hemoglobin consists of a large protein (the globin part) in which four iron-containing **heme** groups are embedded (see Fig. 8.22b). Oxygen can bind at each heme group, so one molecule of hemoglobin binds up to four molecules of O_2 in a series of consecutive equilibria:

$$\mathrm{Hb}(aq) + \mathrm{O_2}(g) \rightleftharpoons \mathrm{Hb(O_2)}(aq) \qquad K_1 = \frac{[\mathrm{Hb(O_2)}]}{[\mathrm{Hb}]P_{\mathrm{O_2}}} = 4.88$$

$$\mathrm{Hb(O_2)}(aq) + \mathrm{O_2}(g) \rightleftharpoons \mathrm{Hb(O_2)_2}(aq) \qquad K_2 = \frac{[\mathrm{Hb(O_2)_2}]}{[\mathrm{HbO_2}]P_{\mathrm{O_2}}} = 15.4$$

$$\mathrm{Hb(O_2)_2}(aq) + \mathrm{O_2}(g) \rightleftharpoons \mathrm{Hb(O_2)_3}(aq) \qquad K_3 = \frac{[\mathrm{Hb(O_2)_3}]}{[\mathrm{Hb(O_2)_2}]P_{\mathrm{O_2}}} = 6.49$$

$$\mathrm{Hb(O_2)_3}(aq) + \mathrm{O_2}(g) \rightleftharpoons \mathrm{Hb(O_2)_4}(aq) \qquad K_4 = \frac{[\mathrm{Hb(O_2)_4}]}{[\mathrm{Hb(O_2)_3}]P_{\mathrm{O_2}}} = 1750$$

The four K's are not equal, and K_4 is far larger than the other three.

Myoglobin is different. The globin portion of myoglobin embeds only one heme group, and each myoglobin molecule can bind only one O_2.

$$\mathrm{Mb}(aq) + \mathrm{O_2}(g) \rightleftharpoons \mathrm{Mb(O_2)}(aq) \qquad K = \frac{[\mathrm{Mb(O_2)}]}{[\mathrm{Mb}]P_{\mathrm{O_2}}} = 271$$

Changing the partial pressure of O_2 should affect the myoglobin equilibrium and all four of the hemoglobin equilibria similarly. Increasing P_{O_2} should shift all of the equilibria to the right; decreasing P_{O_2} should shift them all to the left. One way to check this is to plot the fraction of the binding sites occupied by O_2 as a function of P_{O_2}. Figure 14.5 shows such **fractional saturation** plots for hemoglobin and myoglobin. Clearly, a reduction of P_{O_2} in fact causes less O_2 to be bound, but hemoglobin and myoglobin respond to the reduction in P_{O_2} to very different extents. At $P_{O_2} = 0.13$ atm, both hemoglobin and myoglobin are more than 95% saturated with O_2 at equilibrium. By contrast, at $P_{O_2} = 0.040$ atm, saturation of hemoglobin has been markedly reduced to 55%, while that of myoglobin stays above 90%. The first of these partial pressure values is typical of arterial blood from the lungs, and the second is typical of venous blood. Thus, as P_{O_2} decreases in the capillaries, hemoglobin releases a substantial amount of oxygen, but myoglobin in the nearby cells can take it up. The net result is transfer of O_2 from blood (hemoglobin) to cells (myoglobin).

The S-shaped curve for hemoglobin in Figure 14.5 can be derived mathematically from the different *K*'s for the four equilibria by which hemoglobin binds O_2. The large K_4 means that the affinity of hemoglobin for oxygen rises with uptake of oxygen. From the opposite perspective, we see that loss of the first O_2 from $Hb(O_2)_4$ facilitates loss of more O_2, and the fractional saturation curve for Hb dips below that of Mb. This phenomenon, called "positive cooperativity," originates in structural changes within the hemoglobin molecule as it binds successive molecules of oxygen.

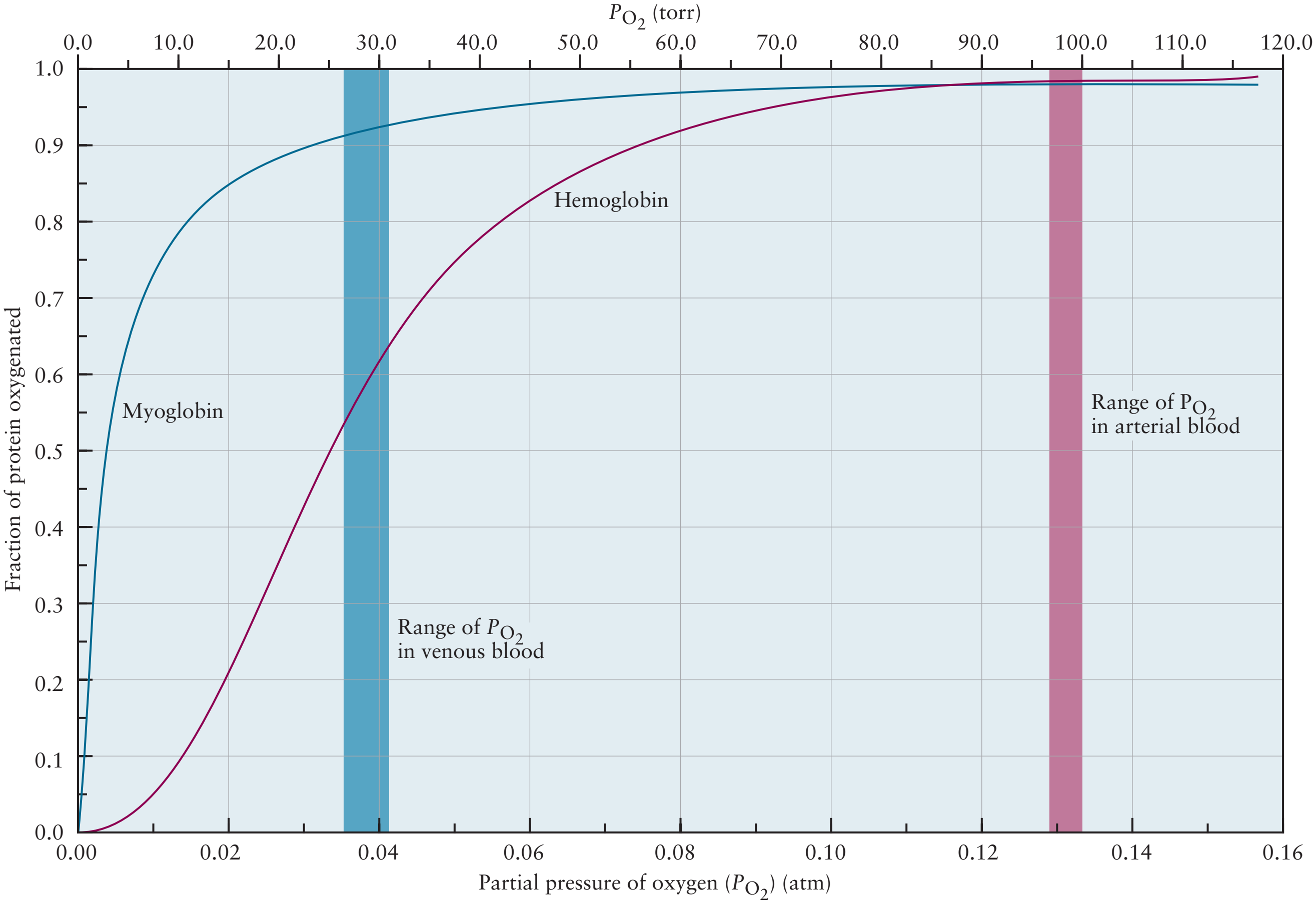


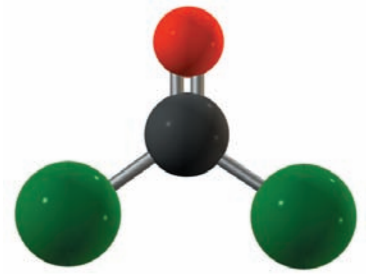
FIGURE 14.5 A plot of the fraction of the binding sites of hemoglobin (red) and myoglobin (blue) that are occupied as a function of the partial pressure of O_2.

14.5 Equilibrium Calculations for Gas-Phase and Heterogeneous Reactions

Equilibrium calculations, used throughout the science of chemistry in both basic and applied work, involve specific procedures. The present section presents these problem-solving techniques in the context of gas-phase and heterogeneous reactions, but they are applicable in *all* equilibrium calculations. We illustrate these calculation methods with several examples that fall into two broad classes: evaluating the equilibrium constant from reaction data, and calculating the amounts of products and reactants present at equilibrium when the equilibrium constant is known.

Evaluating Equilibrium Constants from Reaction Data

In Section 14.3 we showed how to evaluate K from calorimetric data on the pure reactants and products. Occasionally, these thermodynamic data may not be available for a specific reaction, or a quick estimate of the value of K may suffice. In these cases we can evaluate the equilibrium constant from measurements made directly on the reaction mixture. If we can measure the equilibrium partial pressures of all the reactants and products, we can calculate the equilibrium constant by writing the equilibrium expression and substituting the experimental values (in atmospheres) into it. In many cases it is not practical to measure directly the equilibrium partial pressure of each separate reactant and product. Nonetheless, the equilibrium constant can usually be derived from other available data, although the determination is less direct. We illustrate the method in the following two examples.



Phosgene, $COCl_2$, is a chemical intermediate used in making polyurethanes for foams and surface coatings.

EXAMPLE 14.8

Phosgene, $COCl_2$, forms from CO and Cl_2 according to the equilibrium

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

At 600°C, a gas mixture of CO and Cl_2 is prepared that has initial partial pressures (before reaction) of 0.60 atm for CO and 1.10 atm for Cl_2. After the reaction mixture has reached equilibrium, the partial pressure of $COCl_2(g)$ at this temperature is measured to be 0.10 atm. Calculate the equilibrium constant for this reaction. The reaction is carried out in a vessel of fixed volume.

SOLUTION

Only the equilibrium partial pressure of $COCl_2(g)$ and the *initial* partial pressures of the other two gases are given. To find the equilibrium constant, it is necessary to determine the equilibrium partial pressures of CO and Cl_2. To do this, we set up a simple table:

	$CO(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$COCl_2(g)$
Initial partial pressure (atm)	0.60		1.10		0
Change in partial pressure (atm)	?		?		+0.10
Equilibrium partial pressure (atm)	?		?		0.10

Note that the first two lines must add to give the third. We use the relationships built into the balanced chemical equation to fill in the blanks in the table. Because this is the only reaction taking place, every mole of $COCl_2$ produced consumes exactly 1 mol of CO and exactly 1 mol of Cl_2. According to the ideal gas equation, the partial pressures of gases are proportional to the number of moles of each gas present as long as the volume and temperature are held fixed. Therefore, the change in partial pressure of each gas must be proportional to the change in its number of moles as the mixture goes toward equilibrium. If the partial pressure of $COCl_2$ *increases* by 0.10 atm through reaction, the partial pressures of CO and Cl_2 must each *decrease* by 0.10 atm. Inserting these values into the table gives

	$CO(g)$	+	$Cl_2(g)$	$\rightleftarrows$	$COCl_2(g)$
Initial partial pressure (atm)	0.60		1.10		0
Change in partial pressure (atm)	−0.10		−0.10		+0.10
Equilibrium partial pressure (atm)	0.50		1.00		0.10

where the last line was obtained by adding the first two.

We now insert the equilibrium partial pressures into the equilibrium expression to calculate the equilibrium constant:

$$K = \frac{P_{COCl_2}}{(P_{CO})(P_{Cl_2})} = \frac{(0.10)}{(0.50)(1.00)} = 0.20$$

Related Problems: 21, 22, 23, 24

For a reaction in which some of the coefficients in the balanced equation are not equal to 1, deriving expressions for the changes in the partial pressures of the products and reactants requires care. Consider the combustion of ethane at constant volume:

$$2\ C_2H_6(g) + 7\ O_2(g) \rightleftarrows 4\ CO_2(g) + 6\ H_2O(g)$$

If the initial partial pressures are all 1.00 atm and there is a net reaction from left to right in this equation, the table is

	$2\ C_2H_6(g)$	+	$7\ O_2(g)$	$\rightleftarrows$	$4\ CO_2(g)$	+	$6\ H_2O(g)$
Initial partial pressure	1.00		1.00		1.00		1.00
Change in partial pressure	$-2y$		$-7y$		$+4y$		$+6y$
Equilibrium partial pressure	$1.00 - 2y$		$1.00 - 7y$		$1.00 + 4y$		$1.00 + 6y$

If the C_2H_6 partial pressure decreases by $2y$ atm, that of O_2 must decrease by $7y$, because the coefficients in the balanced equation are 2 and 7. The changes in partial pressures of products will have the opposite sign (positive instead of negative), because as reactants disappear, products appear. Their magnitudes are determined according to the coefficients in the balanced equation.

EXAMPLE 14.9

Graphite (a form of solid carbon) is added to a vessel that contains $CO_2(g)$ at a pressure of 0.824 atm at a certain high temperature. The pressure rises due to a reaction that produces $CO(g)$. The total pressure reaches an equilibrium value of 1.366 atm. (**a**) Write a balanced equation for the process. (**b**) Calculate the equilibrium constant.

SOLUTION

(**a**) The reaction can only be the oxidation of C by CO_2 during which the CO_2 is itself reduced to CO. The reaction and its equilibrium expression are written as

$$C(s) + CO_2(g) \rightleftarrows 2\ CO(g) \qquad \frac{(P_{CO})^2}{P_{CO_2}} = K$$

(b) To determine the equilibrium constant, we set up the standard table to describe reaction progress:

	$C(s)$	+	$CO_2(g)$	$\rightleftharpoons$	$2\ CO(g)$
Initial partial pressure (atm)			0.824		0
Change in partial pressure (atm)			$-x$		$+2x$
Equilibrium partial pressure (atm)			$0.824 - x$		$2x$

The total pressure at equilibrium is

$$P_{\text{tot}} = 0.824 \text{ atm} - x + 2x = 0.824 + x = 1.366 \text{ atm}$$

Solving for x gives

$$x = 1.366 - 0.824 = 0.542 \text{ atm}$$

The equilibrium partial pressures of the two gases are

$$P_{\text{CO}} = 2x = 1.084 \text{ atm}$$

$$P_{\text{CO}_2} = 0.824 - 0.542 = 0.282 \text{ atm}$$

The equilibrium constant for the reaction is therefore

$$K = \frac{(1.084)^2}{0.282} = 4.17$$

Related Problems: 25, 26

Calculating Equilibrium Compositions When K Is Known

The law of mass action gives the *form* of the expression for the equilibrium constant for any chemical reaction. We can use these expressions to predict the outcomes of chemical reactions. How to approach the problem depends on the type of experimental data available.

Suppose you are asked to determine the partial pressures of reactants and products at equilibrium, given initial partial pressures of the reactants. This is illustrated by the following example.

EXAMPLE 14.10

Suppose $H_2(g)$ and $I_2(g)$ are sealed in a flask at $T = 400$ K with partial pressures $P_{H_2} = 1.320$ atm and $P_{I_2} = 1.140$ atm. At this temperature H_2 and I_2 do not react rapidly to form $HI(g)$, although after a long enough time they would produce $HI(g)$ at its equilibrium partial pressure. Suppose, instead, that the gases are heated in the sealed flask to 600 K, a temperature at which they quickly reach equilibrium:

$$H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$$

The equilibrium constant for the reaction is 92.6 at 600 K:

$$\frac{P_{\text{HI}}^2}{P_{H_2}P_{I_2}} = 92.6$$

(a) What are the equilibrium values of P_{H_2}, P_{I_2}, and P_{HI} at 600 K?

(b) What percentage of the I_2 originally present has reacted when equilibrium is reached?

SOLUTION

(a) Suppose H_2 and I_2 did *not* react at 600 K. From the ideal gas law at constant volume, their partial pressures would be

$$P^{\circ}_{H_2} = 1.320 \text{ atm} \times \left(\frac{600 \text{ K}}{400 \text{ K}}\right) = 1.980 \text{ atm}$$

$$P^{\circ}_{I_2} = 1.140 \text{ atm} \times \left(\frac{600 \text{ K}}{400 \text{ K}}\right) = 1.710 \text{ atm}$$

Of course, these gases *do* react, and the extent of the reaction can be calculated. To do this, set up a table as in Example 14.8:

	$H_2(g)$	+	$I_2(g)$	$\rightleftarrows$	$2\ HI(g)$
Initial partial pressure (atm)	1.980		1.710		0
Change in partial pressure (atm)	$-x$		$-x$		$+2x$
Equilibrium partial pressure (atm)	$1.980 - x$		$1.710 - x$		$2x$

If the partial pressure of H_2 decreases by x atm as the reaction proceeds, then the partial pressure of I_2 must also decrease by x atm because each mole of H_2 reacts with 1 mol of I_2. By similar reasoning, the partial pressure of HI increases by $2x$ atm: 2 mol of HI forms from each mole of H_2. Inserting the equilibrium partial pressures into the equilibrium expression results in the equation

$$\frac{(2x)^2}{(1.980 - x)(1.710 - x)} = 92.6$$

Multiplying and collecting terms gives

$$88.6x^2 - 341.694x + 313.525 = 0$$

Solving for x using the quadratic formula (see Appendix C) gives

$$x = \frac{-(-341.694) \pm \sqrt{(341.694)^2 - 4(88.6)(313.525)}}{2(88.6)}$$

$$= 1.5044 \text{ atm or } 2.3522 \text{ atm}$$

The second root is physically impossible because it leads to negative answers for the equilibrium partial pressures of the $H_2(g)$ and $I_2(g)$. Discarding it leaves

$$P_{HI} = 2 \times 1.5044 \text{ atm} = 3.0088 \text{ atm}$$

$$P_{H_2} = 1.980 \text{ atm} - 1.5044 \text{ atm} = 0.4756 \text{ atm}$$

$$P_{I_2} = 1.710 \text{ atm} - 1.5044 \text{ atm} = 0.2056 \text{ atm}$$

It is a good idea to check such results by inserting the calculated equilibrium partial pressures back into the equilibrium expression to make sure that the known value of K comes out.

$$\text{Check:} \quad \frac{(3.0088)^2}{(0.4756)(0.2056)} = 92.6$$

As the final step, round off each answer to the correct number of significant digits: $P_{HI} = 3.01$ atm, $P_{H_2} = 0.48$ atm, $P_{I_2} = 0.21$ atm. Rounding off sooner makes the K calculated in the check differ somewhat from 92.6.

(b) The fraction of I_2 that has *not* reacted is the ratio of the number of moles of I_2 present at the end to that present at the beginning. Because neither volume nor temperature changes during the reaction, this equals the ratio of the final partial pressure of I_2 (0.2056 atm) to its initial partial pressure (1.710 atm):

$$\text{percentage unreacted} = \frac{0.2056 \text{ atm}}{1.710 \text{ atm}} \times 100\% = 12\%$$

The percentage that *has* reacted is then 88%.

Related Problems: 27, 28, 29, 30, 31, 32

The concentrations of any products initially present must also be included in equilibrium calculations, as illustrated by the following example.

EXAMPLE 14.11

Hydrogen is made from natural gas (methane) for immediate consumption in industrial processes, such as ammonia production. The first step is called the "steam reforming of methane":

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3\,H_2(g)$$

The equilibrium constant for this reaction is 1.8×10^{-7} at 600 K. Gaseous CH_4, H_2O, and CO are introduced into an evacuated container at 600 K, and their initial partial pressures (before reaction) are 1.40 atm, 2.30 atm, and 1.60 atm, respectively. Determine the partial pressure of $H_2(g)$ that will result at equilibrium.

SOLUTION

The equilibrium expression is

$$\frac{(P_{CO})(P_{H_2})^3}{(P_{CH_4})(P_{H_2O})} = K$$

Set up the table of partial pressures:

	$CH_4(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CO(g)$	+	$3\,H_2(g)$
Initial partial pressure	1.40		2.30		1.60		0
Change in partial pressure	$-y$		$-y$		$+y$		$+3y$
Equilibrium partial pressure	$1.40 - y$		$2.30 - y$		$1.60 + y$		$3y$

Insert the equilibrium partial pressures into the equilibrium expression:

$$\frac{(1.60 + y)(3y)^3}{(1.40 - y)(2.30 - y)} = 1.8 \times 10^{-7}$$

If we expand this equation by multiplying through by the denominator, a polynomial equation of fourth order in y would result, for which the quadratic formula from the preceding problem would be useless. How can we solve the equation?

The equilibrium constant in this case is quite small, so the extent of reaction will also be small. This suggests that y will be a small number relative to the partial pressures of the gases present initially. Let's try the approximation that y can be ignored where it is added to a number that is close to one; that is, let's replace $1.60 + y$ with 1.60 in the preceding equation, and make the same approximation for the two terms in the denominator. When *y multiplies* something, as in the $(3y)^3$ term, of course we cannot set it equal to zero. The result of these steps is the approximate equation

$$\frac{(1.60)(3y)^3}{(1.40)(2.30)} = 1.8 \times 10^{-7}$$

$$y^3 = 1.34 \times 10^{-8}$$

The cube roots of both sides give

$$y = 2.38 \times 10^{-3}$$

This value is indeed small compared with 1.60, 1.40, and 2.30, so our approximation of neglecting y relative to these numbers is justified. Finally, at equilibrium we have

$$P_{H_2} = 3y = 7.1 \times 10^{-3} \text{ atm}$$

Related Problems: 33, 34, 35, 36

Suppose the data for a gas-phase equilibrium are given in terms of concentrations rather than partial pressures. In such cases we convert all concentrations to partial pressures before starting the calculations. Or, we can rewrite the equilibrium expression in terms of concentration variables. The concentration [A] of an ideal gas is related to its partial pressure P_A through

$$[A] = \frac{n_A}{V} = \frac{P_A}{RT}$$

which can be written

$$P_A = RT[A]$$

We can substitute such a relation for each species appearing in the equilibrium expression. It is best to put the factors of $P_{ref} = 1$ atm back into the equilibrium expression to examine the units of the resulting equations. For the general gas-phase reaction

$$aA(g) + bB(g) \rightleftarrows cC(g) + dD(g)$$

the equilibrium expression is

$$\frac{(RT[C]/P_{ref})^c (RT[D]/P_{ref})^d}{(RT[A]/P_{ref})^a (RT[B]/P_{ref})^b} = K$$

Rearranging gives

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = K(\mathrm{RT}/\mathrm{P}_{ref})^{+a+b-c-d}$$

This expression relates concentrations of gas-phase species at equilibrium. If $a + b - c - d = 0$ (that is, if there is no change in the total number of moles of gases in the reaction mixture), the right side of the equilibrium expression reduces to K.

EXAMPLE 14.12

At elevated temperatures, PCl_5 dissociates extensively according to

$$PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$$

At 300°C, the equilibrium constant for this reaction is $K = 11.5$. The concentrations of PCl_3 and Cl_2 at equilibrium in a container at 300°C are both 0.0100 mol L^{-1}. Calculate $[PCl_5]$.

SOLUTION

Two moles of gases are produced for each mole of gas consumed, so RT/P_{ref} must be raised to the power $1 - 2 = -1$. Hence,

$$\frac{[PCl_3][Cl_2]}{[PCl_5]} = K\left(\frac{RT}{P_{ref}}\right)^{-1} = K\left(\frac{P_{ref}}{RT}\right)$$

$$= 11.5 \times \frac{1 \text{ atm}}{(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(573 \text{ K})} = 0.245 \frac{\text{mol}}{\text{L}}$$

Solving this equation for $[PCl_5]$ gives

$$[PCl_5] = \frac{[PCl_3][Cl_2]}{0.245 \text{ mol L}^{-1}} = \frac{(0.0100 \text{ mol L}^{-1})(0.0100 \text{ mol L}^{-1})}{0.245 \text{ mol L}^{-1}}$$

$$= 4.08 \times 10^{-4} \text{ mol L}^{-1}$$

Related Problems: 31, 32

14.6 The Direction of Change in Chemical Reactions: Empirical Description

The specific examples in Section 14.5 illustrate how the law of mass action gives information about the nature of the equilibrium state. The law of mass action also explains and predicts the direction in which a reaction will proceed spontaneously when reactants and products are initially mixed together with arbitrary partial pressures or compositions. This requires a new concept, the reaction quotient Q, which is related to the equilibrium constant. Through the *principle of Le Châtelier* (described below), the mass action law also explains how a reaction in equilibrium responds to an external perturbation.

The Reaction Quotient

The **reaction quotient** Q for a general gas-phase reaction is defined as

$$Q = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

where the partial pressures do *not* necessarily have their equilibrium values. The distinction between Q and K is crucial. The equilibrium constant K is determined by the partial pressures of reactants and products at equilibrium, and it is a constant, dependent only on the temperature. The reaction quotient Q depends on the actual instantaneous partial pressures, whatever they may be; thus, Q changes with time. As the reaction approaches equilibrium, Q approaches K. The initial partial pressures P_A°, P_B°, P_C°, and P_D° give an initial reaction quotient Q_0, whose magnitude relative to K determines the direction in which the reaction will proceed spontaneously toward equilibrium. If Q_0 is *less* than K, then Q must *increase* as time goes on. This requires an increase in the product partial pressures and a decrease in reactant partial pressures; in other words, the reaction proceeds from left to right. If Q_0 is *greater* than K, similar reasoning shows that the reaction will proceed from right to left, with Q *decreasing* with time until it becomes equal to K (Fig. 14.6).

EXAMPLE 14.13

The reaction between nitrogen and hydrogen to produce ammonia

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

is essential in making nitrogen-containing fertilizers. This reaction has an equilibrium constant equal to 1.9×10^{-4} at 400°C. Suppose that 0.10 mol of N_2, 0.040 mol of H_2, and 0.020 mol of NH_3 are sealed in a 1.00-L vessel at 400°C. In which direction will the reaction proceed?

SOLUTION

The initial pressures $P_i = n_iRT/V$ are readily calculated to be

$$P_{N_2} = 5.5 \text{ atm} \qquad P_{H_2} = 2.2 \text{ atm} \qquad P_{NH_3} = 1.1 \text{ atm}$$

The initial numerical value of Q is therefore

$$Q_0 = \frac{(P_{NH_3}^\circ)^2}{P_{N_2}^\circ(P_{H_2}^\circ)^3} = \frac{(1.1)^2}{(5.5)(2.2)^3} = 2.1 \times 10^{-2}$$

Because $Q_0 > K$, the reaction will proceed from right to left and ammonia will dissociate until equilibrium is reached.

Related Problems: 45, 46, 47, 48

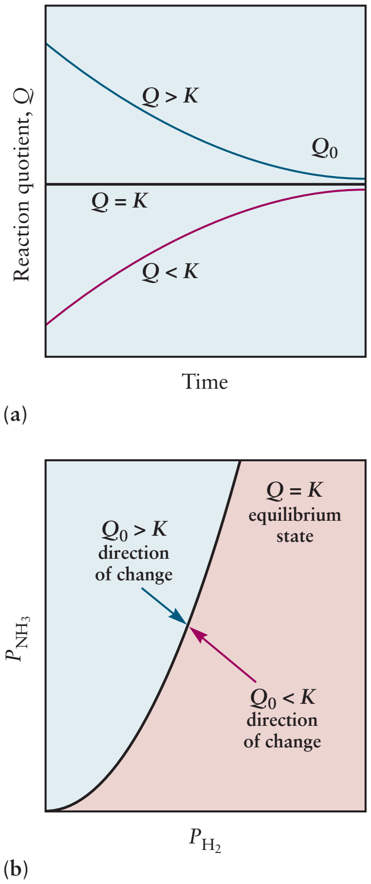


FIGURE 14.6 If nitrogen and hydrogen are mixed in 1 : 3 proportions together with some ammonia, they react according to the chemical equation

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$$

(a) If the initial reaction quotient Q_0 is less than K it increases with time; if it is greater than K, it decreases. (b) With three moles of H_2 available for each mole of N_2, a parabolic curve represents the partial pressures of ammonia and of hydrogen that coexist at equilibrium. From initial nonequilibrium conditions on either side, the partial pressures approach equilibrium along lines with slope −2/3, because three moles of H_2 are consumed to produce two moles of NH_3.

EXAMPLE 14.14

Solid ammonium chloride is in equilibrium with ammonia and hydrogen chloride gases:

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

The equilibrium constant at 275°C is 1.04×10^{-2}.

We place 0.980 g of solid NH_4Cl into a closed vessel with volume 1.000 L and heat to 275°C. (**a**) In what direction does the reaction proceed? (**b**) What is the partial pressure of each gas at equilibrium? (**c**) What is the mass of solid NH_4Cl at equilibrium?

SOLUTION

(**a**) We evaluate the reaction quotient

$$Q = P_{NH_3}P_{HCl}$$

Initially, $Q_0 = 0$ because neither gas is present. By comparison, $K = 1.04 \times 10^{-2}$. Because $Q < K$, the reaction will proceed spontaneously from left to right. Some of the solid NH_4Cl will decompose, and some gaseous NH_3 and HCl will appear in the vessel.

(**b**) We set up the standard table for the equilibrium calculation:

	$NH_4Cl(s)$	$\rightleftharpoons$	$NH_3(g)$	+	$HCl(g)$
Initial partial pressure (atm)			0		0
Change in partial pressure (atm)			$+x$		$+x$
Equilibrium partial pressure (atm)			$+x$		$+x$

Because NH_3 and HCl are formed in equimolar amounts, they will have the same partial pressure at equilibrium. The equilibrium expression is

$$P_{NH_3}P_{HCl} = K = 1.04 \times 10^{-2}$$

$$x^2 = 1.04 \times 10^{-2}$$

$$x = 0.102$$

At equilibrium, the partial pressures are

$$P_{NH_3} = P_{HCl} = 0.102\ \text{atm}$$

(**c**) The number of moles of NH_4Cl that decomposed is equal to the number of moles of each gas produced. We calculate this number, treating the gases as ideal

$$n_{NH_3} = n_{HCl} = \frac{(1.02 \times 10^{-1}\ \text{atm})(1.000\ \text{L})}{(0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1})(548.2\ \text{K})} = 2.268 \times 10^{-3}\ \text{mol}$$

The mass of NH_4Cl consumed is $(2.268 \times 10^{-3}\ \text{mol})(53.49\ \text{g mol}^{-1}) = 0.121$ g. The remaining mass is 0.859 g. The percentage decomposition of the original sample is 12.4%.

Related Problems: 49, 50

External Effects on *K*: Principle of Le Châtelier

Suppose a system at equilibrium is perturbed by some external stress such as a change in volume or temperature or a change in the partial pressure or concentration of one of the reactants or products. How will the system respond? The qualitative answer is embodied in a principle stated by Henri Le Châtelier in 1884:

> *A system in equilibrium that is subjected to a stress will react in a way that tends to counteract the stress.*

Le Châtelier's principle provides a way to predict qualitatively the direction of change of a system under an external perturbation. It relies heavily on *Q* as a predictive tool.

EFFECTS OF CHANGING THE CONCENTRATION OF A REACTANT OR PRODUCT As a simple example, consider what happens when a small quantity of a reactant is added to an equilibrium mixture. The addition of reactant lowers the reaction quotient *Q* below *K* and a net reaction takes place in the forward direction, partially converting reactants to products, until *Q* again equals *K*. The system partially counteracts the stress (the increase in the quantity of one of the reactants) and attains a new equilibrium state. If one of the *products* is added to an equilibrium mixture, *Q* temporarily becomes *greater* than *K* and a net *back* reaction occurs, partially counteracting the imposed stress by reducing the concentration of products (Fig. 14.7).

EXAMPLE 14.15

An equilibrium gas mixture of $H_2(g)$, $I_2(g)$, and $HI(g)$ at 600 *K* has

$$P_{H_2} = 0.4756 \text{ atm} \qquad P_{I_2} = 0.2056 \text{ atm} \qquad P_{HI} = 3.009 \text{ atm}$$

This is essentially the final equilibrium state of Example 14.10. Enough H_2 is added to increase its partial pressure to 2.000 atm at 600 K before any reaction takes place. The mixture then once again reaches equilibrium at 600 K. What are the final partial pressures of the three gases?

SOLUTION

Set up the usual table, in which "initial" now means the moment after the addition of the new H_2 but before it reacts further.

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2\ HI(g)$
Initial partial pressure (atm)	2.000		0.2056		3.009
Change in partial pressure (atm)	$-x$		$-x$		$+2x$
Equilibrium partial pressure (atm)	$2.000 - x$		$0.2056 - x$		$3.009 + 2x$

From Le Châtelier's principle it follows that net reaction to consume H_2 will occur after addition of H_2, and this fact has been used in assigning a negative sign to the change in the partial pressure of H_2 in the table.

Substitution of the equilibrium partial pressures into the equilibrium law gives

$$\frac{(3.009 + 2x)^2}{(2.000 - x)(0.2056 - x)} = 92.6$$

Expansion of this expression results in the quadratic equation

$$88.60x^2 - 216.275x + 29.023 = 0$$

which can be solved to give

$$x = 0.1425 \text{ or } 2.299$$

The second root would lead to negative partial pressures of H_2 and I_2 and is therefore physically impossible. Substitution of the first root into the expressions from the table gives

$$P_{H_2} = 2.000 - 0.1425 = 1.86 \text{ atm}$$

$$P_{I_2} = 0.2056 - 0.1425 = 0.063 \text{ atm}$$

$$P_{HI} = 3.009 + 2(0.1425) = 3.29 \text{ atm}$$

$$\text{Check:} \quad \frac{(3.29)^2}{(1.86)(0.063)} = 92.4$$

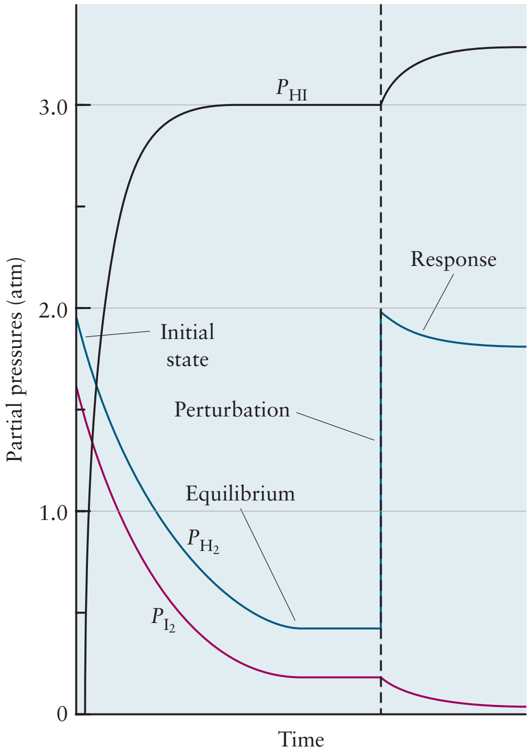


FIGURE 14.7 Partial pressures versus time for the equilibrium

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

The left part of the figure shows the attainment of equilibrium starting from the initial conditions of Example 14.10. Then the equilibrium state is abruptly perturbed by an increase in the partial pressure of H_2 to 2.000 atm. In accordance with Le Châtelier's principle, the system responds (Example 14.15) in such a way as to decrease the partial pressure of H_2—that is, to counteract the perturbation that moved it away from equilibrium in the first place.

When HI is made from the elements, iodine is a much more expensive reactant than hydrogen. It therefore makes sense to add hydrogen to the reaction mixture (as in Example 14.15) to ensure more complete reaction of the iodine. If one of the products is removed from an equilibrium mixture, the reaction will also occur in the forward direction to compensate partially by increasing the partial pressures of products. Most industrial operations are designed in such a way that products can be removed continuously to achieve high overall yields, even for reactions with small equilibrium constants.

EFFECTS OF CHANGING THE VOLUME Le Châtelier's principle also predicts the effect of a change in volume on gas-phase equilibrium. Decreasing the volume of a gaseous system increases its total pressure, and the system responds, if possible, to reduce the total pressure. For example, in the equilibrium

$$2\ P_2(g) \rightleftarrows P_4(g)$$

the reaction shifts in the forward direction when the volume is decreased. This occurs because every two molecules of P_2 consumed produce only one molecule of P_4, thus reducing the total pressure and partially compensating for the external stress caused by the change in volume. In contrast, an *increase* in volume favors reactants over products in this system, and some P_4 dissociates to form P_2 (Fig. 14.8). If there is no difference in the total numbers of gas-phase molecules on the two sides of the equation, then a change in volume has no effect on the equilibrium.

This effect of changing the volume of an equilibrium reacting mixture can also be understood by using the reaction quotient. For the phosphorus equilibrium just described, the reaction quotient is

$$Q = \frac{P_{\mathrm{P}_4}}{(P_{\mathrm{P}_2})^2}$$

Initially, Q_0 equals K. Suppose the volume is then decreased by a factor of 2; because the temperature is unchanged, this initially increases each partial pressure by a factor of 2. Because there are two powers of the pressure in the denominator and only one in the numerator, this decreases Q by a factor of 2, making it lower than K. Reaction must then occur in the forward direction until Q again equals K.

When the volume of a system is decreased, its total pressure increases. Another way to increase the total pressure is to add an inert gas such as argon to the reaction mixture without changing the total volume. In this case the effect on the equilibrium is entirely different. Because the partial pressures of the reactant and product gases are unchanged by an inert gas, adding argon at constant volume has no effect on the position of the equilibrium.

EFFECTS OF CHANGING THE TEMPERATURE Chemical reactions are either **endothermic** (taking up heat from the surroundings) or **exothermic** (giving off heat). Raising the temperature of an equilibrium mixture by adding heat causes reactions to occur in such a way as to absorb some of the added heat. The equilibrium in an endothermic reaction shifts from left to right, while that in an exothermic reaction shifts from right to left, with "products" reacting to give "reactants."

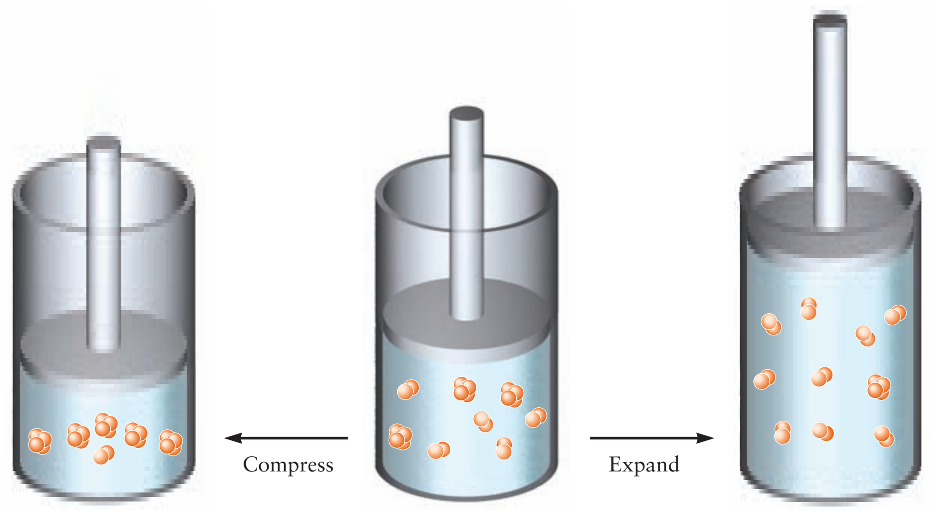


FIGURE 14.8 An equilibrium mixture of P_2 and P_4 (center) is compressed (left). Some P_2 molecules combine to give P_4 molecules, to reduce the total number of molecules and thus the total pressure. If the volume is increased (right), some P_4 molecules dissociate to pairs of P_2 molecules to increase the total number of molecules and the pressure exerted by those molecules.

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FIGURE 14.9 The equilibrium between N_2O_4 and NO_2 depends on temperature. The tube on the right, held in an ice bath at 0°C, contains mostly N_2O_4. Its color is pale because only NO_2 is colored. The deeper color in the tube on the left, which is held at 50°C, reflects the increased NO_2 present in equilibrium at the higher temperature. The tubes contain the same masses of substance, distributed in different ways between NO_2 and N_2O_4.

Equivalently, we can describe the shifts in terms of the effect of temperature on equilibrium constants. The equilibrium constant for an endothermic reaction increases with increasing temperature, while that for an exothermic reaction decreases with increasing temperature.

This effect is illustrated by the equilibrium between nitrogen dioxide (NO_2) and its dimer, dinitrogen tetraoxide (N_2O_4) (briefly considered in Example 9.6) expressed by the chemical equation

$$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$$

Because NO_2 is a brown gas but N_2O_4 is colorless, the equilibrium between them can be studied by observing the color of a tube containing the two gases. At high temperatures, NO_2 predominates and a brown color results; as the temperature is lowered, the partial pressure of N_2O_4 increases and the color fades (Fig. 14.9).

The equilibrium expression for the N_2O_4–NO_2 equilibrium is

$$\frac{P_{N_2O_4}}{(P_{NO_2})^2} = K$$

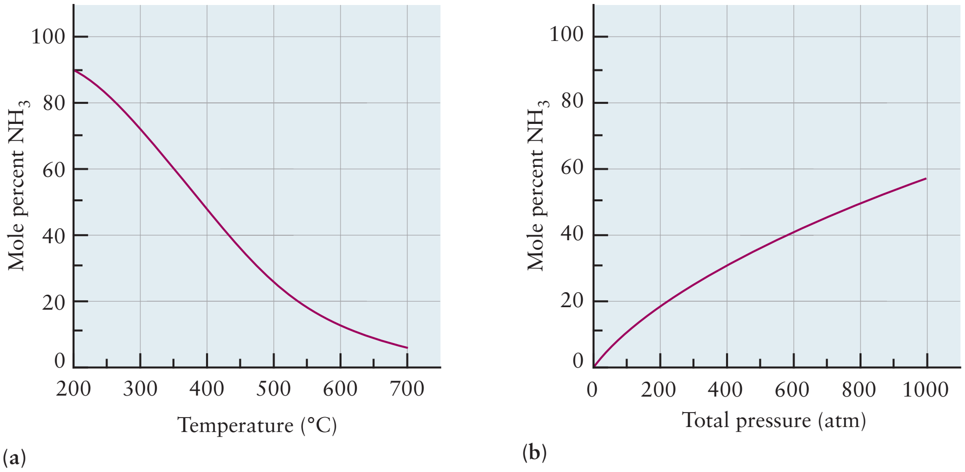
K has the numerical value 8.8 at $T = 25°C$, provided the partial pressures of N_2O_4 and NO_2 are expressed in atmospheres. This reaction is exothermic ($\Delta H = -58.02\ kJ\ mol^{-1}$ at 298 K) because energy must be liberated when dimers are formed. Consequently, K decreases as the temperature T increases, so the amount of N_2O_4 present for a given partial pressure of NO_2 falls with increasing temperature as the dimer dissociates at elevated temperatures.

MAXIMIZING THE YIELD OF A REACTION As an application of Le Châtelier's principle, consider the reaction

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$$

which is the basis of the industrial synthesis of ammonia. Because this reaction is exothermic, the yield of ammonia is increased by working at as low a temperature as possible (Fig. 14.10a). At too low a temperature, the reaction is very slow, so a compromise temperature near 500°C is typically used. Because the number of moles of gas decreases as the reaction occurs, the yield of product is enhanced by decreasing the volume of the reaction vessel. Typically, total pressures of 150 to 300 atm are used (see Fig. 14.10b), although some plants work at up to 900 atm of pressure. Even at high pressures, the yield of ammonia is usually only 15% to 20% because the equilibrium constant is so small. To overcome this, ammonia plants operate in a cyclic process in which the gas mixture is cooled after ammonia is produced so that the ammonia liquefies (its boiling point is much higher than those of nitrogen and hydrogen) and is removed from the reaction vessel. Continuous removal of products helps drive the reaction to completion.

FIGURE 14.10 (a) The equilibrium mole percentage of ammonia in a 1:3 mixture of N_2 and H_2 varies with temperature; low temperatures favor high yields of NH_3. The data shown correspond to a fixed total pressure of 300 atm. (b) At a fixed temperature (here, 500°C), the yield of NH_3 increases with increasing total pressure.



14.7 The Direction of Change in Chemical Reactions: Thermodynamic Explanation

The specific examples in Section 14.5 demonstrate that when $K \gg 1$ the reaction has progressed far toward products, and when $K \ll 1$ the reaction has remained near reactants. The empirical discussion in Section 14.6 shows how the reaction quotient Q and the principle of Le Châtelier can predict the direction of spontaneous reaction and the response of an equilibrium state to an external perturbation. Here, we use the thermodynamic description of K from Section 14.3 to provide the thermodynamic basis for these results obtained empirically in Sections 14.5 and 14.6. We identify those thermodynamic factors that determine the magnitude of K. We also provide a thermodynamic criterion for predicting the direction in which a reaction proceeds from a given initial condition.

The Magnitude of the Equilibrium Constant

The expression connecting the standard Gibbs free energy change and the equilibrium constant can be rewritten as

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

so that

$$K = \exp\left[\frac{-\Delta G^\circ}{RT}\right] = \exp\left[\frac{\Delta S^\circ}{R}\right] \exp\left[\frac{-\Delta H^\circ}{RT}\right]$$

Here K is large (favoring the products) if ΔS° is positive and large and ΔH° is negative and large. In other words, an increase in the number of microstates ($\Delta S^\circ > 0$) and a decrease in enthalpy ($\Delta H^\circ < 0$) both favor a large K. Thus, the same factors that favor reaction spontaneity by making ΔG° negative also favor a large K if they can make ΔG° large in magnitude as well as negative in sign. If ΔH° and ΔS° have the *same* sign, the value of K will be a compromise between one effect that raises K and another that lowers it.

Free Energy Changes and the Reaction Quotient

The direction in which a spontaneous chemical reaction proceeds after it is initiated with a given initial concentration of products and reactants is the direction in which $\Delta G < 0$. If the initial condition is "to the left" of the equilibrium state, products will be formed at the expense of reactants; if the initial condition is "to the right" of the equilibrium state, products will be converted back to reactants. This criterion can be made quantitative and expressed in terms of the initial concentrations as follows.

Proceeding as in Section 14.3, we find ΔG for the general gas-phase reaction

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

to be

$$\Delta G = \Delta G^\circ + RT \ln \left[\frac{(P_\text{C}/P_\text{ref})^c (P_\text{D}/P_\text{ref})^d}{(P_\text{A}/P_\text{ref})^a (P_\text{B}/P_\text{ref})^b}\right]$$

At equilibrium, where $\Delta G = 0$, the combination of partial pressures appearing inside the brackets becomes the equilibrium constant, K. Away from equilibrium, this combination of partial pressures is the reaction quotient Q, introduced in Section 14.6:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

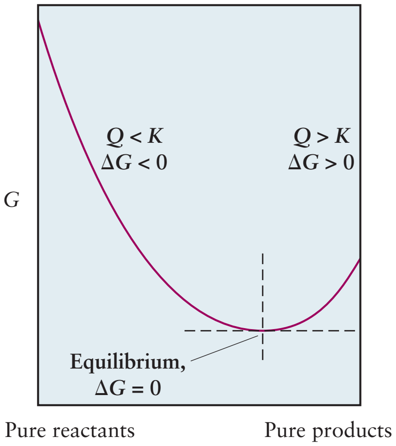


FIGURE 14.11 The free energy of a reaction system is plotted against its progress from pure reactants (left) to pure products (right). Equilibrium comes at the minimum of the curve. To the reactant side of equilibrium, $\Delta G < 0$ and $Q < K$. A reaction mixture with initial condition in this range will spontaneously move toward equilibrium by converting more reactants into products. To the product side of equilibrium, $\Delta G > 0$ and $Q > K$. A reaction mixture prepared in this range will spontaneously move toward equilibrium by converting products back into reactants.

The equilibrium constant can be substituted for $\Delta G°$ in this equation to obtain a very useful relation between ΔG, K, and Q as follows:

$$\begin{aligned}\Delta G &= \Delta G° + RT\ln Q = -RT\ln K + RT\ln Q\\ &= RT\ln(Q/K)\end{aligned} \qquad [14.10]$$

If the reaction quotient Q is *less* than K, $\Delta G < 0$ and the reaction will proceed spontaneously as written, from left to right. If $Q > K$, then $\Delta G > 0$ and the *reverse* reaction (right to left) will occur spontaneously until equilibrium is reached. These conditions are represented schematically in Figure 14.11. The second law of thermodynamics thus provides a very useful criterion for the direction of reaction in terms of the initial value of the reaction quotient.

There exists a deep relationship between Figure 14.6, which represents actual events occurring in the laboratory, and Figure 14.11, which represents the thermodynamic driving force (that is, the Gibbs free energy) governing these events.

Temperature Dependence of Equilibrium Constants

Le Châtelier's principle is a qualitative way of describing the *stability* of equilibrium states against sudden perturbations in concentration, pressure, and temperature. The responses of the system to all three effects can be described quantitatively by thermodynamics. Here we describe the effect of temperature, which is the most useful of these quantitative descriptions.

The temperature dependence of the equilibrium constant is determined by the equation

$$-RT\ln K = \Delta G° = \Delta H° - T\Delta S°$$

If $\Delta H°$ and $\Delta S°$ are independent of temperature, then all the temperature dependence of K lies in the factor of T and the equation can be used to relate the values of K at two different temperatures, as follows. At least over a limited temperature range, $\Delta H°$ and $\Delta S°$ do not vary much with temperature. To the extent that their temperature dependence may be neglected, it is evident that $\ln K$ is a linear function of $1/T$ as shown in Figure 14.12.

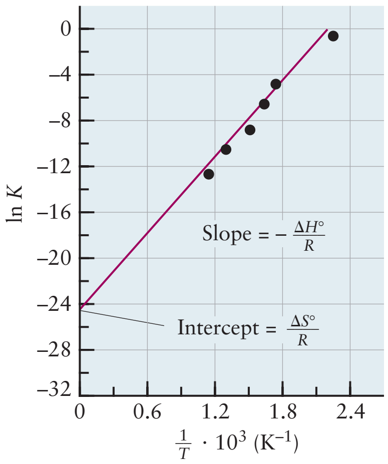


FIGURE 14.12 The temperature dependence of the equilibrium constant for the reaction

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Experimental data are shown by points.

$$\ln K = -\frac{\Delta G°}{RT} = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \qquad [14.11]$$

A graph of $\ln K$ against $1/T$ is approximately a straight line with slope $-\Delta H°/R$ and intercept $\Delta S°/R$ (see Fig. 14.12). If the value of K is known for one temperature and $\Delta H°$ is also known, K can be calculated for other temperatures.

In addition to the graphical method, an equation can be obtained to connect the values of K at two different temperatures. Let K_1 and K_2 be the equilibrium constants for a reaction at temperatures T_1 and T_2, respectively. Then

$$\ln K_2 = -\frac{\Delta H°}{RT_2} + \frac{\Delta S°}{R}$$

$$\ln K_1 = -\frac{\Delta H°}{RT_1} + \frac{\Delta S°}{R}$$

Subtracting the second equation from the first gives

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H°}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad [14.12]$$

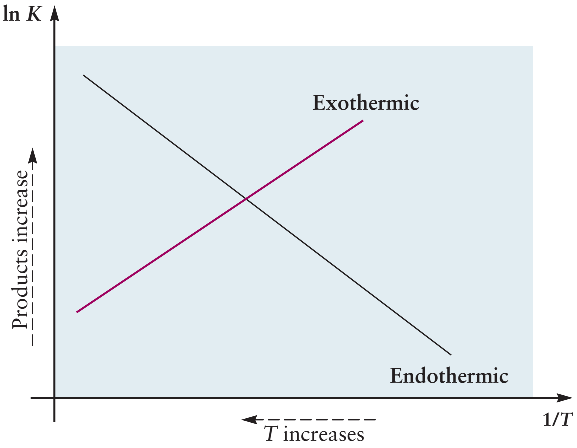


FIGURE 14.13 Sketch of ln *K* against 1/*T* for an exothermic reaction and for an endothermic reaction, as predicted by thermodynamics. Temperature increases to the left on this diagram. As *T* increases, *K* for the endothermic reaction increases and *K* for the exothermic reaction decreases in accordance with the principle of Le Châtelier.

This is known as the **van't Hoff equation** after the Dutch chemist Jacobus van't Hoff. Given $\Delta H°$ and *K* at one temperature, we can use the equation to calculate *K* at another temperature, within the approximation that $\Delta H°$ and $\Delta S°$ are independent of temperature. Alternatively, we can use it to determine $\Delta H°$ without a calorimeter if the values of *K* are known at several temperatures.

The effect of a temperature change on the equilibrium constant depends on the sign of $\Delta H°$. If $\Delta H°$ is negative (the reaction is exothermic, giving off energy as heat), then increasing the temperature *reduces* *K*. If $\Delta H°$ is positive (the reaction is endothermic, taking up energy as heat), then increasing the temperature *increases* *K*. These observations obtained from thermodynamics provide the quantitative basis for Le Châtelier's principle (Fig. 14.13).

EXAMPLE 14.16

Calculate *K* for the equilibrium of Example 14.4 at $T = 400$ K, assuming $\Delta H°$ to be approximately independent of temperature over the range from 298 to 400 K.

SOLUTION

The first step is to calculate $\Delta H°$ for the reaction. Appendix D provides data to calculate

$$\Delta H° = -155.52 \text{ kJ}$$

From the van't Hoff equation,

$$\ln\left(\frac{K_{400}}{K_{298}}\right) = -\frac{\Delta H°}{R}\left[\frac{1}{400 \text{ K}} - \frac{1}{298 \text{ K}}\right]$$

$$= \frac{155{,}520 \text{ J mol}^{-1}}{8.315 \text{ J K}^{-1} \text{ mol}^{-1}}\left[\frac{1}{400 \text{ K}} - \frac{1}{298 \text{ K}}\right] = -16.01$$

$$\frac{K_{400}}{K_{298}} = e^{-16.01} = 1.1 \times 10^{-7}$$

Taking K_{298} to be 1.8×10^{18} (from Example 14.4) gives

$$K_{400} = (1.8 \times 10^{18})(1.1 \times 10^{-7}) = 2.0 \times 10^{11}$$

Because the reaction is exothermic, an increase in temperature reduces the equilibrium constant.

An alternative way to do this calculation would be to determine both $\Delta H°$ and $\Delta S°$ and from them to calculate ΔG at 400 K.

Related Problems: 61, 62, 63, 64, 65, 66

Temperature Dependence of Vapor Pressure

Suppose pure liquid water is in equilibrium with its vapor at temperature T:

$$H_2O(\ell) \rightleftharpoons H_2O(g) \qquad P_{H_2O(g)} = K$$

The temperature dependence of K (and therefore of the vapor pressure $P_{H_2O(g)}$) is a special case of the van't Hoff equation. If ΔH_{vap} and ΔS_{vap} are approximately independent of temperature, then from the van't Hoff equation,

$$\ln\left(\frac{K_2}{K_1}\right) = \ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

where P_2 and P_1 are the vapor pressures at temperatures T_2 and T_1. From this equation, the vapor pressure at any given temperature can be estimated if its value at some other temperature is known and if the enthalpy of vaporization is also known.

At the normal boiling point of a substance, T_b, the vapor pressure is 1 atm. If T_1 is taken to correspond to T_b and T_2 to some other temperature T, the van't Hoff equation is

$$\ln P = -\frac{\Delta H_{vap}}{R}\left[\frac{1}{T} - \frac{1}{T_b}\right] \qquad [14.13]$$

where P is the vapor pressure at temperature T, expressed in atmospheres.

EXAMPLE 14.17

The ΔH_{vap} for water is 40.66 kJ mol^{-1} at the normal boiling point, $T_b = 373$ K. Assuming ΔH_{vap} and ΔS_{vap} are approximately independent of temperature from 50°C to 100°C, estimate the vapor pressure of water at 50°C (323 K).

SOLUTION

$$\ln P_{323} = \frac{-40660 \text{ J mol}^{-1}}{8.315 \text{ J K}^{-1}\text{ mol}^{-1}}\left[\frac{1}{323 \text{ K}} - \frac{1}{373 \text{ K}}\right] = -2.03$$

$$P_{323} = 0.13 \text{ atm}$$

This differs slightly from the experimental value, 0.1217 atm, because ΔH_{vap} *does* change with temperature, an effect that was neglected in the approximate calculation.

Related Problems: 67, 68

14.8 Distribution of a Single Species between Immiscible Phases: Extraction and Separation Processes

An important type of heterogeneous equilibrium involves partitioning a solute species between two immiscible solvent phases. Such equilibria are used in many separation processes in chemical research and in industry.

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FIGURE 14.14 Iodine is dissolved in water and poured on top of carbon tetrachloride in a separatory funnel (left). After the funnel is shaken (right), the iodine reaches a partition equilibrium between the upper (aqueous) phase and the lower (CCl_4) phase. The deeper color in the lower phase indicates that iodine dissolves preferentially in the denser CCl_4 phase.

Suppose two immiscible liquids, such as water and carbon tetrachloride, are put in a container. "Immiscible" means mutually insoluble; these liquids separate into two phases with the less dense liquid, in this case water, lying on top of the other liquid. A visible boundary, the meniscus, separates the two phases. If a solute such as iodine is added to the mixture and the vessel is shaken to distribute the iodine through the container (Fig. 14.14), the iodine is partitioned between the two phases at equilibrium with a characteristic concentration ratio, the **partition coefficient** K. This is the equilibrium constant for the process

$$I_2(aq) \rightleftarrows I_2(CCl_4)$$

and can be written as

$$\frac{[I_2]_{CCl_4}}{[I_2]_{aq}} = K$$

in which $[I_2]_{CCl_4}$ and $[I_2]_{aq}$ are the concentrations (in moles per liter) of I_2 in the CCl_4 and aqueous phases, respectively. At 25°C, K has the value 85 for this equilibrium. The fact that K is greater than 1 shows that iodine is more soluble in CCl_4 than in water. If iodide ion (I^-) is dissolved in the water, then it can react with iodine to form the triiodide ion I_3^-:

$$I_2(aq) + I^-(aq) \longrightarrow I_3^-(aq)$$

This consumes $I_2(aq)$ and, by Le Châtelier's principle, causes more I_2 in the first equilibrium to move from the CCl_4 phase to the aqueous phase.

Extraction Processes

Extraction takes advantage of the partitioning of a solute between two immiscible solvents to remove that solute from one solvent into another. Suppose iodine is present as a contaminant in water that also contains other solutes that are insoluble in carbon tetrachloride. In such a case, most of the iodine could be removed by shaking the aqueous solution with CCl_4, allowing the two phases to separate, and then pouring off the water layer from the heavier layer of carbon tetrachloride. The greater the equilibrium constant for the partition of a solute from the original solvent into the extracting solvent, the more complete such a separation will be.

EXAMPLE 14.18

An aqueous solution has an iodine concentration of 2.00×10^{-3} M. Calculate the percentage of iodine remaining in the aqueous phase after extraction of 0.100 L of this aqueous solution with 0.050 L of CCl_4 at 25°C.

SOLUTION

The number of moles of I_2 present is

$$(2.00 \times 10^{-3} \text{ mol L}^{-1})(0.100\ L) = 2.00 \times 10^{-4} \text{ mol}$$

Suppose that y mol remains in the aqueous phase and $(2.00 \times 10^{-4} - y)$ mol passes into the CCl_4 phase. Then

$$\frac{[I_2]_{CCl_4}}{[I_2]_{aq}} = K = 85$$

$$= \frac{(2.00 \times 10^{-4} - y)/0.050}{y/0.100}$$

$$= \frac{2(2.00 \times 10^{-4} - y)}{y}$$

Note that the volumes of the two solvents used are unchanged because they are immiscible. Solving for y gives

$$y = 4.6 \times 10^{-6} \text{ mol}$$

The fraction remaining in the aqueous phase is $(4.6 \times 10^{-6})/(2.0 \times 10^{-4}) = 0.023$, or 2.3%. Additional extractions could be carried out to remove more of the I_2 from the aqueous phase.

Related Problems: 71, 72, 73, 74

One extraction process used industrially on a large scale is the purification of sodium hydroxide for use in the manufacture of rayon. The sodium hydroxide produced by electrolysis typically contains 1% sodium chloride and 0.1% sodium chlorate as impurities. If a concentrated aqueous solution of sodium hydroxide is extracted with liquid ammonia, the NaCl and $NaClO_3$ are partitioned into the ammonia phase in preference over the aqueous phase. The heavier aqueous phase is added to the top of an extraction vessel filled with ammonia, and equilibrium is reached as droplets of it settle through the ammonia phase to the bottom. This procedure reduces impurity concentrations in the sodium hydroxide solution to about 0.08% NaCl and 0.0002% $NaClO_3$.

Chromatographic Separations

Partition equilibria are the basis of an important class of separation techniques called **chromatography.** This word comes from the Greek root *chroma,* meaning "color," and was chosen because the original chromatographic separations involved colored substances. The technique can be applied to a variety of mixtures of substances.

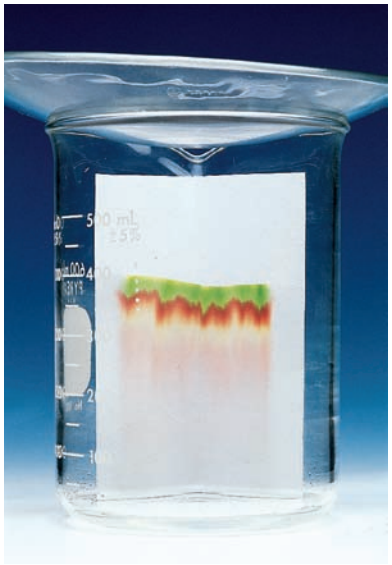
Chromatography is a continuous extraction process in which solute species are exchanged between two phases. One, the mobile phase, moves with respect to the other, stationary phase. The partition ratio K of a solute A between the stationary and mobile phases is

$$\frac{[\text{A}]_{\text{stationary}}}{[\text{A}]_{\text{mobile}}} = K$$

As the mobile phase containing solute passes over the stationary phase, the solute molecules move between the two phases. True equilibrium is never fully established because the motion of the fluid phase continually brings fresh solvent into contact with the stationary phase. Nevertheless, the partition coefficient K provides a guide to the behavior of a particular solute. The greater K is, the more time the solute spends in the stationary phase and therefore the slower its progress through the separation system. Solutes with different values of K are separated by their different rates of travel.

Different types of chromatography use different mobile and stationary phases; Table 14.1 lists some of the most important. **Column chromatography** (Fig. 14.15) uses a tube packed with a porous material, often a silica gel on which water has been adsorbed. Water is therefore the stationary liquid phase in this case. Other solvents such as pyridine or benzene are used in the mobile phase; in some cases it is most efficient to use different solvents in succession to separate the components of a solute mixture. As the solute fractions reach the bottom of the column, they are separated for analysis or use. Column chromatography is important in industry because it is easily increased from laboratory to production scale.

Gas–liquid chromatography (Fig. 14.16) is one of the most important separation techniques for modern chemical research. The stationary phase is again a liquid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Paper chromatography separates a line of ink, drawn across the bottom of the paper, into its component colors. As the water rises through the paper, the different components of the ink are attracted differently to the water and the paper and are separated.

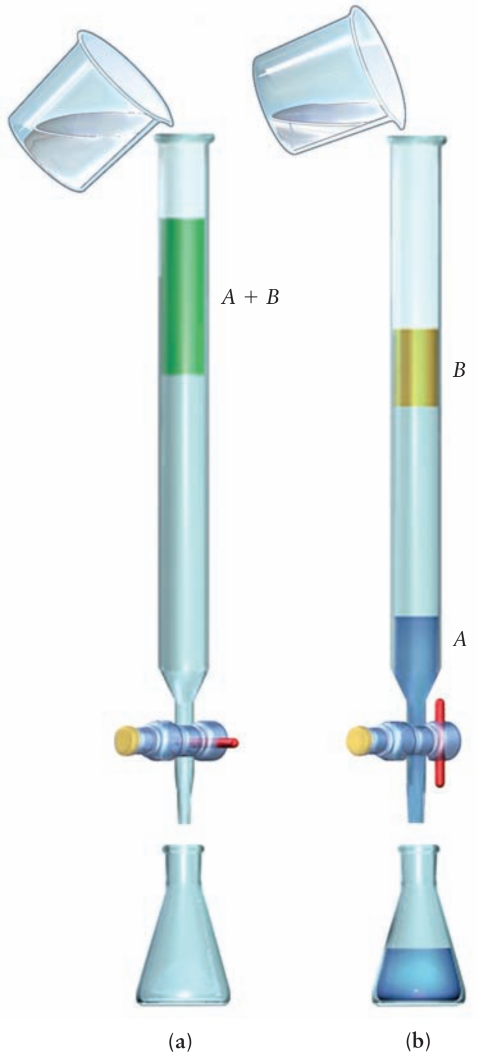

FIGURE 14.15 (a) In a column chromatograph, the top of the column is loaded with a mixture of solutes to be separated (green). (b) Upon addition of solvent, the different solutes travel at different rates, giving rise to bands. The separate fractions can be collected in different flasks for use or analysis.

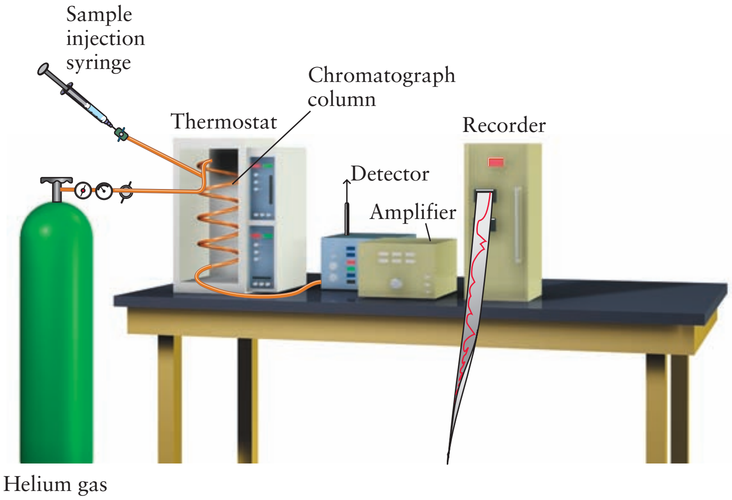

FIGURE 14.16 In a gas–liquid chromatograph, the sample is vaporized and passes through a column, carried in a stream of an inert gas such as helium or nitrogen. The residence time of any substance on the column depends on its partition coefficient from the vapor to the liquid in the column. A species leaving the column at a given time can be detected by a variety of techniques. The result is a gas chromatogram, with a peak corresponding to each substance in the mixture.

TABLE 14.1 Chromatographic Separation Techniques[†]

Name	Mobile Phase	Stationary Phase
Gas–liquid	Gas	Liquid adsorbed on a porous solid in a tube
Gas–solid	Gas	Porous solid in a tube
Column	Liquid	Liquid adsorbed on a porous solid in a tubular column
Paper	Liquid	Liquid held in the pores of a thick paper
Thin layer	Liquid	Liquid or solid; solid is held on glass plate and liquid may be adsorbed on it
Ion exchange	Liquid	Solid (finely divided ion-exchange resin) in a tubular column

[†] Adapted from D. A. Skoog and D. M. West, *Analytical Chemistry* (Saunders College Publishing, Philadelphia, 1980), Table 18-1.

adsorbed on a porous solid, but the mobile phase is now gaseous. The sample is vaporized and passes through the column, carried in a stream of an inert gas such as helium or nitrogen. The residence time in the column depends on the partition coefficient of the solute species, allowing an efficient separation of mixtures. The solute leaving the column at a given time can be detected by a variety of techniques that produce a **gas chromatogram** with a peak corresponding to each solute species in the mixture. Gas–liquid chromatography is widely used for separating the products of organic reactions. It can also be used to determine the purity of substances, because even very small amounts of impurities appear clearly as separate peaks in the chromatogram. The technique is important in the separation and identification of trace amounts of possibly toxic substances in environmental and biological samples. Amounts on the order of parts per trillion (10^{-12} g in a 1-g sample) can be detected and identified.

CHAPTER SUMMARY

Most chemical reactions do not go to completion. They arrive at the equilibrium state, after which there is no further net change in the amount of products or reactants. At the microscopic level, the reaction continues in both forward and reverse directions, at equal rates in these opposing directions. So, chemical equilibrium—which we measure at the macroscopic level—is characterized by a dynamical balance of events on the microscopic level. At the equilibrium state, concentrations of products and reactants always satisfy the mass action law, and so are related by the equilibrium constant. The equilibrium constant is a unique property of each chemical reaction. Knowledge of the equilibrium constant enables us to calculate the equilibrium concentrations of products and reactants that result from any set of initial concentrations for that reaction. Equilibrium calculations have enormous predictive power for interpreting and optimizing the outcome of chemical reactions. Thermodynamics explains all the empirical observations of chemical equilibrium and provides means for quantitative predictions. Thermodynamics explains the form of the mass action law, shows how to calculate the equilibrium constant from tabulations of Gibbs free energy for products and reactants, explains the temperature dependence of the equilibrium constant, and predicts the direction of change in response to any disturbance of the equilibrium state.


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A stockpile of sulfur near chemical plants in Los Angeles.

CUMULATIVE EXERCISE

This cumulative exercise is divided into two parts. Readers who have not yet studied thermodynamics should stop after Part 1; those who have studied thermodynamics should continue with Part 2.

Cumulative Exercise Part 1

Sulfuric Acid

Sulfuric acid is produced in larger volume than any other chemical and has a tremendous number of applications, ranging from fertilizer manufacture to metal treatment and chemical synthesis.

The modern industrial production of sulfuric acid involves three steps, for which the balanced chemical equations are:

1. $S(s) + O_2(g) \rightleftharpoons SO_2(g)$

2. $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

3. $SO_3(g) + H_2O(\ell) \rightleftharpoons H_2SO_4(\ell)$

(a) Write an equilibrium expression for each of these steps, with equilibrium constants K_1, K_2, and K_3.

(b) If these reactions could be carried out at 25°C, the equilibrium constants would be 3.9×10^{52}, 2.6×10^{12}, and 2.6×10^{14}. Write a balanced equation for the overall reaction and calculate its equilibrium constant at 25°C.

(c) Although the products of all three equilibria are strongly favored at 25°C [See the data given in part (b)], reactions 1 and 2 occur too slowly to be practical; they must be carried out at elevated temperatures. At 700°C, the partial pressures of SO_2, O_2, and SO_3 in an equilibrium mixture are measured to be 2.23 atm, 1.14 atm, and 6.26 atm, respectively. Calculate K_2 at 700°C.

(d) At 300°C, K_2 has the value 1.3×10^4. Suppose some SO_3 is introduced into an evacuated vessel at an initial partial pressure of 0.89 atm. Calculate the partial pressure of SO_2 that will be reached at equilibrium, assuming that only reaction 2 takes place under these conditions. (*Hint:* K_2 is large enough that you can assume the fraction of SO_3 dissociated is very small.)

(e) Some SO_2 is placed in a flask and heated with oxygen to 600°C, at which point $K_2 = 9.5$. At equilibrium, 62% of it has reacted to give SO_3. Calculate the partial pressure of oxygen at equilibrium in this reaction mixture.

(f) Equal numbers of moles of SO_2, O_2, and SO_3 are mixed and heated to 600°C, where their total pressure before reaction is 0.090 atm. Will reaction 2 occur from right to left or from left to right? Will the total pressure increase or decrease during the course of the reaction?

(g) Reactions 1 and 3 are both exothermic. State the effects on equilibria 1 and 3 of increasing the temperature and of decreasing the volume. (*Note:* A change in volume has little effect on liquids and solids taking part in a reaction.)

Answers

(a) $\frac{P_{SO_2}}{P_{O_2}} = K_1 \qquad \frac{P_{SO_3}}{P_{SO_2}P_{O_2}^{1/2}} = K_2 \qquad \frac{1}{P_{SO_3}} = K_3$

(b) $S(s) + \frac{3}{2}O_2(g) + H_2O(\ell) \rightleftharpoons H_2SO_4(\ell)$; $K = K_1K_2K_3 = 2.2 \times 10^{79}$

(c) K_2 is 2.63.

(d) The SO_2 partial pressure is 2.1×10^{-3} atm.

(e) The O_2 partial pressure is 0.029 atm.

(f) Left to right; pressure will decrease

(g) Increasing the temperature will shift both equilibria to the left. Decreasing the volume will not affect equilibrium 1 and will shift equilibrium 3 to the right.

Cumulative Exercise Part 2

We continue with examination of reactions 1, 2, and 3 in the production of sulfuric acid.

(h) Calculate $\Delta G°$ for each reaction at 25°C. (Standard state of sulfur is rhombic.)

(i) Write a balanced equation for the overall reaction, and calculate its value of $\Delta G°$ at 25°C.

(j) Part (h) shows all three reactions are spontaneous at 25°C. Nonetheless, reactions 1 and 2 occur too slowly at 25°C to be practical; they must be carried out at higher temperatures. Calculate $\Delta G°$ for 1, 2, and 3 at 700°C.

(k) Determine the highest temperature at which all three reactions are spontaneous.

Answers

(h) At 25°C: $\Delta G_1^\circ = -300.19 \text{ kJ mol}^{-1}$; $\Delta G_2^\circ = -70.86 \text{ kJ mol}^{-1}$; $\Delta G_3^\circ = -81.64 \text{ kJ mol}^{-1}$

(i) $S(s) + \frac{3}{2}O_2(g) + H_2O(\ell) \rightleftharpoons H_2SO_4(\ell)$; $\Delta G_{\text{net}}^\circ = -452.89 \text{ kJ mol}^{-1}$

(j) At 700°C: $\Delta G_1^\circ = -307.81 \text{ kJ mol}^{-1}$; $\Delta G_2^\circ = -7.47 \text{ kJ mol}^{-1}$; $\Delta G_3^\circ = +32.64 \text{ kJ mol}^{-1}$

(k) Because reaction 1 has $\Delta H° < 0$ and $\Delta S° > 0$, it is spontaneous at all temperatures. Because both reaction 2 and reaction 3 have $\Delta H° < 0$ and $\Delta S° < 0$, each is spontaneous at temperatures below the temperature T^* at which $\Delta G = 0$. With the higher ratio of $\Delta S°$ to $\Delta H°$, reaction 3 is the first to become nonspontaneous, at $T^* = 508°\text{C}$.

CHAPTER REVIEW

Fundamental Aspects of Chemical Equilibrium

- Approach to chemical equilibrium
  The equilibrium state for a particular reaction at a particular temperature is the same regardless of whether it is approached from reactants or from products.
- Characteristics of the equilibrium state
  No macroscopic evidence of change
  Reached through a spontaneous process
  Dynamic balance between forward and reverse processes
  The same regardless of direction of approach

The Law of Mass Action for Gas-Phase Reactions and Solution Reactions

- $\dfrac{P_C^c P_D^d}{P_A^a P_B^b} = K$
- $\dfrac{[C]^c[D]^d}{[A]^a[B]^b} = K$
- In these equations we describe reaction quantities as follows:
  The concentrations of gases are expressed in partial pressures in atm.
  The concentrations of solutes are expressed in moles per liter.
  The concentrations of pure liquids and pure solids are set equal to one, as is the concentration of the solvent in a dilute solution.
  Partial pressures and concentrations of products appear in the numerator and those of the reactants in the denominator; each is raised to a power equal to its stoichiometric coefficient in the balanced reaction.

Thermodynamic Description of the Equilibrium State

- Pressure dependence of the Gibbs Free Energy for ideal gas species

$$\Delta G = \Delta(H - TS) = \Delta H - T\,\Delta S = -T\,\Delta S \text{ for constant T}$$

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right) = nR \ln\left(\frac{P_1}{P_2}\right) = -nR \ln\left(\frac{P_2}{P_1}\right)$$

$\Delta G = nRT \ln P$ if P is expressed in atm.

- To obtain the equilibrium expression for ideal gas reactions:
  - Take reactants from initial pressure to 1 atm.
  - Run reaction at 1 atm.
  - Take products from 1 atm to final pressure

$$\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3$$
$$-\Delta G^\circ = RT \ln K(T)$$

  Calculate K by calculating ΔG° from tables of ΔG_f° for reactants and products.

- The equilibrium expression for solution and heterogeneous reactions is developed in the same way.
  - Represent each species by its activity.
  - Replace the activity with its limiting form of partial pressure or concentration.
  - For pure solid or liquid products or reactants in their reference states set the activity equal to 1.
  - Calculate K by calculating ΔG° from tables of ΔG_f° for reactants and products, paying careful attention to reference state for each species.

The Law of Mass Action for Related and Simultaneous Reactions

- $K_{\text{reverse}} = -K_{\text{forward}}$
- K (equation multiplied by n) $= K^n$
- $K_3 = K_1K_2 \ldots$ when a series of reactions is added to give an overall reaction.
- $K_3 = K_1/K_2 \ldots$ if one reaction in a series is subtracted to give an overall reaction.

Equilibrium Calculations for Gas-Phase and Heterogeneous Reactions

- Evaluate equilibrium constants from reaction data.
  - Substitute experimental results into equilibrium constant expression.
- Calculate equilibrium compositions when K is known.
  - Procedures are illustrated in Example 14.1.

Empirical Description of the Direction of Change in Chemical Reactions

- The reaction quotient

$$Q = \frac{P_C^c P_D^d}{P_A^a P_D^d} \text{ is defined for any point along the reaction}$$
$$Q < K \Rightarrow \text{reaction moves to the right}$$
$$Q = K \Rightarrow \text{equilibrium}$$
$$Q > K \Rightarrow \text{reaction moves to the left}$$

- Le Châtelier's Principle—A system in equilibrium that is subjected to a stress will react in a way to counteract the stress. Several specific cases are:
  - Stress: increase concentration or pressure of species A.
  - Response: reaction will move in appropriate direction to decrease A.
  - Stress: increase pressure.
  - Response: reaction will move in the direction that gives fewer molecules in order to decrease the pressure.
  - Stress: decrease volume. (Same as increase pressure.)
  - Response: reaction moves in the direction that gives fewer molecules in order to decrease the pressure
  - Stress: increase temperature.
  - Response: reaction moves in appropriate direction to absorb head and decrease the temperature.
  - Endothermic reactions move to the right as T increases.
  - Exothermic reactions move to the left as T increases.

Thermodynamic Explanation of the Direction of Change in Chemical Reactions

- Temperature Dependence of Equilibrium Constants

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H°}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

- Temperature Dependence of Vapor Pressure

$$\ln P = -\frac{\Delta H_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Distribution of a Species between Immiscible Phases

- Methods for extracting a chemical species from preparative mixtures in order to analyze and purify
- Distribution between phases is a form of the mass action law, and is fully described by the methods of chemical equilibrium.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Describe the nature of the equilibrium state in chemical reactions (Section 14.1).
2. Set up the equilibrium expression for homogeneous reactions in the gas phase and in solution, and for heterogeneous reactions (Section 14.2, Problems 1–12).
3. Relate the equilibrium constant of a reaction to its standard Gibbs free energy change (Section 14.3, Problems 13–16).
4. Combine equilibrium constants for individual reactions to obtain net equilibrium constants for combined reactions (Section 14.4, Problems 17–20).
5. Calculate equilibrium constants from experimental measurements of partial and total pressures (Section 14.5, Problems 21–26).
6. Calculate the equilibrium partial pressures of all species involved in a gas-phase chemical or gas-solid reaction from the initial pressure(s) of the reactants (Section 14.5, Problems 27–32).
7. Relate concentrations to partial pressures in equilibrium calculations (Section 14.5, Problems 37–38).
8. Determine the direction in which a chemical reaction will proceed spontaneously by calculating its reaction quotient (Section 14.6, Problems 45–46).
9. State Le Châtelier's principle and give several applications (Section 14.6, Problems 47–58).
10. Relate the change in the equilibrium constant of a reaction with temperature to its standard enthalpy change (Section 14.7, Problems 59–70).
11. Use the law of mass action to explain the distribution of a solute between two immiscible solvents (Section 14.8, Problems 71–74).
12. Outline the basis for separation of compounds by partition chromatography (Section 14.8).

KEY EQUATIONS

$$\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} = K$$ **(Section 14.2)**

$$\frac{[C]^c[D]^d}{[A]^c[B]^b} = K$$ **(Section 14.2)**

$$\Delta G = nRT \ln \left(\frac{P_2}{P_1}\right)$$ (Section 14.3)

$$\Delta G = nRT \ln \left(\frac{P}{P_{\text{ref}}}\right) = nRT \ln P$$ (Section 14.3)

$$-\Delta G° = RT \ln K(T)$$ (Section 14.3)

$$\frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b} = K$$ (Section 14.3)

$$\Delta G = \Delta G° + RT \ln Q = -RT \ln K + RT \ln Q$$
$$= RT \ln (Q/K)$$ (Section 14.7)

$$\ln K = -\frac{\Delta G°}{RT} = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}$$ (Section 14.7)

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H°}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$ (Section 14.7)

$$\ln P = -\frac{\Delta H_{\text{vap}}}{R}\left[\frac{1}{T} - \frac{1}{T_b}\right]$$ (Section 14.7)

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

The Empirical Law of Mass Action

1. Write equilibrium expressions for the following gas-phase reactions.
   (a) $2\ H_2(g) + O_2(g) \rightleftarrows 2\ H_2O(g)$
   (b) $Xe(g) + 3\ F_2(g) \rightleftarrows XeF_6(g)$
   (c) $2\ C_6H_6(g) + 15\ O_2(g) \rightleftarrows 12\ CO_2(g) + 6\ H_2O(g)$

2. Write equilibrium expressions for the following gas-phase reactions.
   (a) $2\ Cl_2(g) + O_2(g) \rightleftarrows 2\ Cl_2O(g)$
   (b) $N_2(g) + O_2(g) + Br_2(g) \rightleftarrows 2\ NOBr(g)$
   (c) $C_3H_8(g) + 5\ O_2(g) \rightleftarrows 3\ CO_2(g) + 4\ H_2O(g)$

3. At a moderately elevated temperature, phosphoryl chloride ($POCl_3$) can be produced in the vapor phase from the gaseous elements. Write a balanced chemical equation and an equilibrium expression for this system. Note that gaseous phosphorus consists of P_4 molecules at moderate temperatures.

4. If confined at high temperature, ammonia and oxygen quickly react and come to equilibrium with their products, water vapor and nitrogen oxide. Write a balanced chemical equation and an equilibrium expression for this system.

5. An important step in the industrial production of hydrogen is the reaction of carbon monoxide with water:

$$CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$$

   (a) Use the law of mass action to write the equilibrium expression for this reaction.
   (b) At 500°C, the equilibrium constant for this reaction is 3.9. Suppose that the equilibrium partial pressures of CO and H_2O are both 0.10 atm and that of CO_2 is 0.70 atm. Calculate the equilibrium partial pressure of $H_2(g)$.

6. Phosgene ($COCl_2$) is an important intermediate in the manufacture of certain plastics. It is produced by the reaction

$$CO(g) + Cl_2(g) \rightleftarrows COCl_2(g)$$

   (a) Use the law of mass action to write the equilibrium expression for this reaction.
   (b) At 600°C, the equilibrium constant for this reaction is 0.20. Calculate the partial pressure of phosgene in equilibrium with a mixture of CO (at 0.0020 atm) and Cl_2 (at 0.00030 atm).

7. N_2O_4 is soluble in the solvent cyclohexane; however, dissolution does not prevent N_2O_4 from breaking down to give NO_2 according to the equation

$$N_2O_{4(\text{cyclohexane})} \rightleftarrows 2\ NO_{2(\text{cyclohexane})}$$

An effort to compare this solution equilibrium with the similar equilibrium in the gas gave the following actual experimental data at 20°C:

$[N_2O_4]$ (mol L^{-1})	$[NO_2]$ (mol L^{-1})
0.190×10^{-3}	2.80×10^{-3}
0.686×10^{-3}	5.20×10^{-3}
1.54×10^{-3}	7.26×10^{-3}
2.55×10^{-3}	10.4×10^{-3}
3.75×10^{-3}	11.7×10^{-3}
7.86×10^{-3}	17.3×10^{-3}
11.9×10^{-3}	21.0×10^{-3}

   (a) Graph the *square* of the concentration of NO_2 versus the concentration of N_2O_4.
   (b) Compute the average equilibrium constant of this reaction.

8. NO_2 is soluble in carbon tetrachloride (CCl_4). As it dissolves, it dimerizes to give N_2O_4 according to the equation

$$2\ NO_{2(CCl_4)} \rightleftharpoons N_2O_{4(CCl_4)}$$

A study of this equilibrium gave the following experimental data at 20°C:

$[N_2O_4]$ (mol L^{-1})	$[NO_2]$ (mol L^{-1})
0.192×10^{-3}	2.68×10^{-3}
0.721×10^{-3}	4.96×10^{-3}
1.61×10^{-3}	7.39×10^{-3}
2.67×10^{-3}	10.2×10^{-3}
3.95×10^{-3}	11.0×10^{-3}
7.90×10^{-3}	16.6×10^{-3}
11.9×10^{-3}	21.4×10^{-3}

(a) Graph the concentration of N_2O_4 versus the *square* of the concentration of NO_2.
(b) Compute the average equilibrium constant of this reaction.

9. Using the law of mass action, write the equilibrium expression for each of the following reactions.
(a) $8\ H_2(g) + S_8(s) \rightleftharpoons 8\ H_2S(g)$
(b) $C(s) + H_2O(\ell) + Cl_2(g) \rightleftharpoons COCl_2(g) + H_2(g)$
(c) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
(d) $3\ C_2H_2(g) \rightleftharpoons C_6H_6(\ell)$

10. Using the law of mass action, write the equilibrium expression for each of the following reactions.
(a) $3\ C_2H_2(g) + 3\ H_2(g) \rightleftharpoons C_6H_{12}(\ell)$
(b) $CO_2(g) + C(s) \rightleftharpoons 2\ CO(g)$
(c) $CF_4(g) + 2\ H_2O(\ell) \rightleftharpoons CO_2(g) + 4\ HF(g)$
(d) $K_2NiF_6(s) + TiF_4(s) \rightleftharpoons K_2TiF_6(s) + NiF_2(s) + F_2(g)$

11. Using the law of mass action, write the equilibrium expression for each of the following reactions.
(a) $Zn(s) + 2\ Ag^+(aq) \rightleftharpoons Zn^{2+}(aq) + 2\ Ag(s)$
(b) $VO_4^{3-}(aq) + H_2O(\ell) \rightleftharpoons VO_3(OH)^{2-}(aq) + OH^-(aq)$
(c) $2\ As(OH)_6^{3-}(aq) + 6\ CO_2(g) \rightleftharpoons As_2O_3(s) + 6\ HCO_3^-(aq) + 3\ H_2O(\ell)$

12. Using the law of mass action, write the equilibrium expression for each of the following reactions.
(a) $6\ I^-(aq) + 2\ MnO_4^-(aq) + 4\ H_2O(\ell) \rightleftharpoons 3\ I_2(aq) + 2\ MnO_2(s) + 8\ OH^-(aq)$
(b) $2\ Cu^{2+}(aq) + 4\ I^-(aq) \rightleftharpoons 2\ CuI(s) + I_2(aq)$
(c) $\frac{1}{2}\ O_2(g) + Sn^{2+}(aq) + 3\ H_2O(\ell) \rightleftharpoons SnO_2(s) + 2\ H_3O^+(aq)$

Thermodynamic Description of the Equilibrium State

13. Calculate $\Delta G°$ and the equilibrium constant K at 25°C for the reaction

$$2\ NH_3(g) + \tfrac{7}{2}\ O_2(g) \rightleftharpoons 2\ NO_2(g) + 3\ H_2O(g)$$

using data in Appendix D.

14. Write a reaction for the dehydrogenation of gaseous ethane (C_2H_6) to acetylene (C_2H_2). Calculate $\Delta G°$ and the equilibrium constant for this reaction at 25°C, using data from Appendix D.

15. Use the thermodynamic data from Appendix D to calculate the equilibrium constant at 25°C for the following reactions:
(a) $SO_2(g) + \frac{1}{2}\ O_2(g) \rightleftharpoons SO_3(g)$
(b) $3\ Fe_2O_3(s) \rightleftharpoons 2\ Fe_3O_4(s) + \frac{1}{2}\ O_2(g)$
(c) $CuCl_2(s) \rightleftharpoons Cu^{2+}(aq) + 2\ Cl^-(aq)$

Write the equilibrium expression for each reaction.

16. Use the thermodynamic data from Appendix D to calculate equilibrium constants at 25°C for the following reactions.
(a) $H_2(g) + N_2(g) + 2\ O_2(g) \rightleftharpoons 2\ HNO_2(g)$
(b) $Ca(OH)_2(s) \rightleftharpoons CaO(s) + H_2O(g)$
(c) $Zn^{2+}(aq) + 4\ NH_3(aq) \rightleftharpoons Zn(NH_3)_4^{2+}(aq)$

Write the equilibrium expression for each reaction.

The Law of Mass Action for Related and Simultaneous Equilibria

17. At a certain temperature, the value of the equilibrium constant for the reaction

$$CS_2(g) + 3\ O_2(g) \rightleftharpoons CO_2(g) + 2\ SO_2(g)$$

is K_1. How is K_1 related to the equilibrium constant K_2 for the related equilibrium

$$\tfrac{1}{3}\ CS_2(g) + O_2(g) \rightleftharpoons \tfrac{1}{3}\ CO_2(g) + \tfrac{2}{3}\ SO_2(g)$$

at the same temperature?

18. At 25°C, the equilibrium constant for the reaction

$$6\ ClO_3F(g) \rightleftharpoons 2\ ClF(g) + 4\ ClO(g) + 7\ O_2(g) + 2\ F_2(g)$$

is 32.6. Calculate the equilibrium constant at 25°C for the reaction

$$\tfrac{1}{3}\ ClF(g) + \tfrac{2}{3}\ ClO(g) + \tfrac{7}{6}\ O_2(g) + \tfrac{1}{3}\ F_2(g) \rightleftharpoons ClO_3F(g)$$

19. Suppose that K_1 and K_2 are the respective equilibrium constants for the two reactions

$$XeF_6(g) + H_2O(g) \rightleftharpoons XeOF_4(g) + 2\ HF(g)$$

$$XeO_4(g) + XeF_6(g) \rightleftharpoons XeOF_4(g) + XeO_3F_2(g)$$

Give the equilibrium constant for the reaction

$$XeO_4(g) + 2\ HF(g) \rightleftharpoons XeO_3F_2(g) + H_2O(g)$$

in terms of K_1 and K_2.

20. At 1330 K, germanium(II) oxide (GeO) and tungsten(VI) oxide (W_2O_6) are both gases. The following two equilibria are established simultaneously:

$$2\ GeO(g) + W_2O_6(g) \rightleftharpoons 2\ GeWO_4(g)$$

$$GeO(g) + W_2O_6(g) \rightleftharpoons GeW_2O_7(g)$$

The equilibrium constants for the two are respectively 7.0×10^3 and 38×10^3. Compute K for the reaction

$$GeO(g) + GeW_2O_7(g) \rightleftharpoons 2\ GeWO_4(g)$$

Equilibrium Calculations for Gas-Phase and Heterogeneous Reactions

21. At 454 K, $Al_2Cl_6(g)$ reacts to form $Al_3Cl_9(g)$ according to the equation

$$3\ Al_2Cl_6(g) \rightleftharpoons 2\ Al_3Cl_9(g)$$

In an experiment at this temperature, the equilibrium partial pressure of $Al_2Cl_6(g)$ is 1.00 atm and the equilibrium partial pressure of $Al_3Cl_9(g)$ is 1.02×10^{-2} atm. Compute the equilibrium constant of the preceding reaction at 454 K.

22. At 298 K, $F_3SSF(g)$ decomposes partially to $SF_2(g)$. At equilibrium, the partial pressure of $SF_2(g)$ is 1.1×10^{-4} atm and the partial pressure of F_3SSF is 0.0484 atm.
(a) Write a balanced equilibrium equation to represent this reaction.
(b) Compute the equilibrium constant corresponding to the equation you wrote.

23. The compound 1,3-di-*t*-butylcyclohexane exists in two forms that are known as the chair and boat conformations because their molecular structures resemble those objects. Equilibrium exists between the two forms, represented by the equation

$$\text{chair} \rightleftharpoons \text{boat}$$

At 580 K, 6.42% of the molecules are in the chair form. Calculate the equilibrium constant for the preceding reaction as written.

24. At 248°C and a total pressure of 1.000 atm, the fractional dissociation of $SbCl_5$ is 0.718 for the reaction

$$SbCl_5(g) \rightleftharpoons SbCl_3(g) + Cl_2(g)$$

This means that 718 of every 1000 molecules of $SbCl_5$ originally present have dissociated. Calculate the equilibrium constant.

25. Sulfuryl chloride (SO_2Cl_2) is a colorless liquid that boils at 69°C. Above this temperature, the vapors dissociate into sulfur dioxide and chlorine:

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

This reaction is slow at 100°C, but it is accelerated by the presence of some $FeCl_3$ (which does not affect the final position of the equilibrium). In an experiment, 3.174 g of $SO_2Cl_2(\ell)$ and a small amount of solid $FeCl_3$ are put into an evacuated 1.000-L flask, which is then sealed and heated to 100°C. The total pressure in the flask at that temperature is found to be 1.30 atm.
(a) Calculate the partial pressure of each of the three gases present.
(b) Calculate the equilibrium constant at this temperature.

26. A certain amount of NOBr(*g*) is sealed in a flask, and the temperature is raised to 350 K. The following equilibrium is established:

$$NOBr(g) \rightleftharpoons NO(g) + \tfrac{1}{2}\,Br_2(g)$$

The total pressure in the flask when equilibrium is reached at this temperature is 0.675 atm, and the vapor density is 2.219 g L^{-1}.
(a) Calculate the partial pressure of each species.
(b) Calculate the equilibrium constant at this temperature.

27. The dehydrogenation of benzyl alcohol to make the flavoring agent benzaldehyde is an equilibrium process described by the equation

$$C_6H_5CH_2OH(g) \rightleftharpoons C_6H_5CHO(g) + H_2(g)$$

At 523 K, the value of its equilibrium constant is $K = 0.558$.
(a) Suppose 1.20 g of benzyl alcohol is placed in a 2.00-L vessel and heated to 523 K. What is the partial pressure of benzaldehyde when equilibrium is attained?
(b) What fraction of benzyl alcohol is dissociated into products at equilibrium?

28. Isopropyl alcohol can dissociate into acetone and hydrogen:

$$(CH_3)_2CHOH(g) \rightleftharpoons (CH_3)_2CO(g) + H_2(g)$$

At 179°C, the equilibrium constant for this dehydrogenation reaction is 0.444.
(a) If 10.00 g of isopropyl alcohol is placed in a 10.00-L vessel and heated to 179°C, what is the partial pressure of acetone when equilibrium is attained?
(b) What fraction of isopropyl alcohol is dissociated at equilibrium?

29. A weighed quantity of $PCl_5(s)$ is sealed in a 100.0-cm^3 glass bulb to which a pressure gauge is attached. The bulb is heated to 250°C, and the gauge shows that the pressure in the bulb rises to 0.895 atm. At this temperature, the solid PCl_5 is all vaporized and also partially dissociated into $Cl_2(g)$ and $PCl_3(g)$ according to the equation

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

At 250°C, $K = 2.15$ for this reaction. Assume that the contents of the bulb are at equilibrium and calculate the partial pressure of the three different chemical species in the vessel.

30. Suppose 93.0 g of HI(*g*) is placed in a glass vessel and heated to 1107 K. At this temperature, equilibrium is quickly established between HI(*g*) and its decomposition products, $H_2(g)$ and $I_2(g)$:

$$2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

The equilibrium constant at 1107 K is 0.0259, and the total pressure at equilibrium is observed to equal 6.45 atm. Calculate the equilibrium partial pressures of HI(*g*), $H_2(g)$, and $I_2(g)$.

31. The equilibrium constant at 350 K for the reaction

$$Br_2(g) + I_2(g) \rightleftharpoons 2\ IBr(g)$$

has a value of 322. Bromine at an initial partial pressure of 0.0500 atm is mixed with iodine at an initial partial pressure of 0.0400 atm and held at 350 K until equilibrium is reached. Calculate the equilibrium partial pressure of each of the gases.

32. The equilibrium constant for the reaction of fluorine and oxygen to form oxygen difluoride (OF_2) is 40.1 at 298 K:

$$F_2(g) + \tfrac{1}{2}\,O_2(g) \rightleftharpoons OF_2(g)$$

Suppose some OF_2 is introduced into an evacuated container at 298 K and allowed to dissociate until its partial pressure reaches an equilibrium value of 1.00 atm. Calculate the equilibrium partial pressures of F_2 and O_2 in the container.

33. At 25°C, the equilibrium constant for the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$$

is 4.2×10^{-31}. Suppose a container is filled with nitrogen (at an initial partial pressure of 0.41 atm), oxygen (at an initial partial pressure of 0.59 atm), and nitrogen oxide (at an initial partial pressure of 0.22 atm). Calculate the partial pressures of all three gases after equilibrium is reached at this temperature.

34. At 25°C, the equilibrium constant for the reaction

$$2\ NO_2(g) \rightleftharpoons 2\ NO(g) + O_2(g)$$

is 5.9×10^{-13}. Suppose a container is filled with nitrogen dioxide at an initial partial pressure of 0.89 atm. Calculate the partial pressures of all three gases after equilibrium is reached at this temperature.

* **35.** The equilibrium constant for the synthesis of ammonia

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

has the value $K = 6.78 \times 10^5$ at 25°C. Calculate the equilibrium partial pressures of $N_2(g)$, $H_2(g)$, and $NH_3(g)$ at 25°C if the total pressure is 1.00 atm and the H:N atom ratio in the system is 3:1. (*Hint:* Try the approximation that P_{N_2} and $P_{H_2} \ll P_{NH_3}$ and see if the resulting equations are simplified.)

* **36.** At 400°C, $K = 3.19 \times 10^{-4}$ for the reaction in problem 35. Repeat the calculation for P_{N_2}, P_{H_2}, and P_{NH_3}, assuming the same total pressure and composition. (*Hint:* Try the approximation that $P_{NH_3} \ll P_{N_2}$ and P_{H_2} and see if the resulting equations are simplified.)

37. Calculate the concentration of phosgene ($COCl_2$) that will be present at 600°C in equilibrium with carbon monoxide (at a concentration of 2.3×10^{-4} mol L^{-1}) and chlorine (at a concentration of 1.7×10^{-2} mol L^{-1}). (Use the data of problem 6.)

38. The reaction

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

has an equilibrium constant at 100°C of 2.40. Calculate the concentration of SO_2 that will be present at 100°C in equilibrium with SO_2Cl_2 (at a concentration of 3.6×10^{-4} mol L^{-1}) and chlorine (at a concentration of 6.9×10^{-3} mol L^{-1}).

39. At 298 K, the equilibrium constant for the reaction

$$Fe_2O_3(s) + 3\,H_2(g) \rightleftharpoons 2\,Fe(s) + 3\,H_2O(\ell)$$

is 4.0×10^{-6}, and that for

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(\ell)$$

is 3.2×10^{-4}. Suppose some solid Fe_2O_3, solid Fe, and liquid H_2O are brought into equilibrium with $CO(g)$ and $CO_2(g)$ in a closed container at 298 K. Calculate the ratio of the partial pressure of $CO(g)$ to that of $CO_2(g)$ at equilibrium.

40. A sample of ammonium carbamate placed in a glass vessel at 25°C undergoes the reaction

$$NH_4OCONH_2(s) \rightleftharpoons 2\,NH_3(g) + CO_2(g)$$

The total pressure of gases in equilibrium with the solid is found to be 0.115 atm.

(a) Calculate the partial pressures of NH_3 and CO_2.
(b) Calculate the equilibrium constant at 25°C.

41. The equilibrium constant for the reaction

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

at 340°C is $K = 4.0$.

(a) If the partial pressure of ammonia is $P_{NH_3} = 0.80$ atm and solid ammonium chloride is present, what is the equilibrium partial pressure of hydrogen chloride at 340°C?
(b) An excess of solid NH_4Cl is added to a container filled with ammonia at 340°C and a pressure of 1.50 atm. Calculate the pressures of $NH_3(g)$ and $HCl(g)$ reached at equilibrium.

42. The equilibrium constant for the reaction

$$H_2(g) + I_2(s) \rightleftharpoons 2\,HI(g)$$

at 25°C is $K = 0.345$.

(a) If the partial pressure of hydrogen is $P_{H_2} = 1.00$ atm and solid iodine is present, what is the equilibrium partial pressure of hydrogen iodide, P_{HI}, at 25°C?
(b) An excess of solid I_2 is added to a container filled with hydrogen at 25°C and a pressure of 4.00 atm. Calculate the pressures of $H_2(g)$ and $HI(g)$ reached at equilibrium.

43. Pure solid NH_4HSe is placed in an evacuated container at 24.8°C. Eventually, the pressure above the solid reaches the equilibrium pressure 0.0184 atm due to the reaction

$$NH_4HSe(s) \rightleftharpoons NH_3(g) + H_2Se(g)$$

(a) Calculate the equilibrium constant of this reaction at 24.8°C.
(b) In a different container, the partial pressure of $NH_3(g)$ in equilibrium with $NH_4HSe(s)$ at 24.8°C is 0.0252 atm. What is the partial pressure of $H_2Se(g)$?

44. The total pressure of the gases in equilibrium with solid sodium hydrogen carbonate at 110°C is 1.648 atm, corresponding to the reaction

$$2\,NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

($NaHCO_3$ is used in dry chemical fire extinguishers because the products of this decomposition reaction smother the fire.)

(a) Calculate the equilibrium constant at 110°C.
(b) What is the partial pressure of water vapor in equilibrium with $NaHCO_3(s)$ at 110°C if the partial pressure of $CO_2(g)$ is 0.800 atm?

The Direction of Change in Chemical Reactions: Empirical Description

45. Some Al_2Cl_6 (at a partial pressure of 0.473 atm) is placed in a closed container at 454 K with some Al_3Cl_9 (at a partial pressure of 1.02×10^{-2} atm). Enough argon is added to raise the total pressure to 1.00 atm.

(a) Calculate the initial reaction quotient for the reaction

$$3\,Al_2Cl_6(g) \rightleftharpoons 2\,Al_3Cl_9(g)$$

(b) As the gas mixture reaches equilibrium, will there be net production or consumption of Al_3Cl_9? (Use the data given in problem 21.)

46. Some SF_2 (at a partial pressure of 2.3×10^{-4} atm) is placed in a closed container at 298 K with some F_3SSF (at a partial pressure of 0.0484 atm). Enough argon is added to raise the total pressure to 1.000 atm.

(a) Calculate the initial reaction quotient for the decomposition of F_3SSF to SF_2.
(b) As the gas mixture reaches equilibrium, will there be net formation or dissociation of F_3SSF? (Use the data given in problem 22.)

47. The progress of the reaction

$$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$$

can be monitored visually by following changes in the color of the reaction mixture (Br_2 is reddish brown, and H_2 and

HBr are colorless). A gas mixture is prepared at 700 K, in which 0.40 atm is the initial partial pressure of both H_2 and Br_2 and 0.90 atm is the initial partial pressure of HBr. The color of this mixture then fades as the reaction progresses toward equilibrium. Give a condition that must be satisfied by the equilibrium constant K (for example, it must be greater than or smaller than a given number).

48. Recall from our discussion of the NO_2–N_2O_4 equilibrium that NO_2 has a brownish color. At elevated temperatures, NO_2 reacts with CO according to

$$NO_2(g) + CO(g) \rightleftharpoons NO(g) + CO_2(g)$$

The other three gases taking part in this reaction are colorless. When a gas mixture is prepared at 500 K, in which 3.4 atm is the initial partial pressure of both NO_2 and CO, and 1.4 atm is the partial pressure of both NO and CO_2, the brown color of the mixture is observed to fade as the reaction progresses toward equilibrium. Give a condition that must be satisfied by the equilibrium constant K (for example, it must be greater than or smaller than a given number).

49. The equilibrium constant for the "water gas" reaction

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

is $K = 2.6$ at a temperature of 1000 K. Calculate the reaction quotient Q for each of the following conditions, and state which direction the reaction shifts in coming to equilibrium.

(a) $P_{H_2O} = 0.600$ atm; $P_{CO} = 1.525$ atm; $P_{H_2} = 0.805$ atm
(b) $P_{H_2O} = 0.724$ atm; $P_{CO} = 1.714$ atm; $P_{H_2} = 1.383$ atm

50. The equilibrium constant for the reaction

$$H_2S(g) + I_2(g) \rightleftharpoons 2\,HI(g) + S(s)$$

at 110°C is equal to 0.0023. Calculate the reaction quotient Q for each of the following conditions and determine whether solid sulfur is consumed or produced as the reaction comes to equilibrium.

(a) $P_{I_2} = 0.461$ atm; $P_{H_2S} = 0.050$ atm; $P_{HI} = 0.0$ atm
(b) $P_{I_2} = 0.461$ atm; $P_{H_2S} = 0.050$ atm; $P_{HI} = 9.0$ atm

51. At $T = 1200°C$ the reaction

$$P_4(g) \rightleftharpoons 2\,P_2(g)$$

has an equilibrium constant $K = 0.612$.

(a) Suppose the initial partial pressure of P_4 is 5.00 atm and that of P_2 is 2.00 atm. Calculate the reaction quotient Q and state whether the reaction proceeds to the right or to the left as equilibrium is approached.
(b) Calculate the partial pressures at equilibrium.
(c) If the volume of the system is then increased, will there be net formation or net dissociation of P_4?

52. At $T = 100°C$ the reaction

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

has an equilibrium constant $K = 2.4$.

(a) Suppose the initial partial pressure of SO_2Cl_2 is 1.20 atm, and $P_{SO_2} = P_{Cl_2} = 0$. Calculate the reaction quotient Q and state whether the reaction proceeds to the right or to the left as equilibrium is approached.
(b) Calculate the partial pressures at equilibrium.
(c) If the volume of the system is then decreased, will there be net formation or net dissociation of SO_2Cl_2?

53. Explain the effect of each of the following stresses on the position of the following equilibrium:

$$3\,NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$$

The reaction as written is exothermic.

(a) $N_2O(g)$ is added to the equilibrium mixture without change of volume or temperature.
(b) The volume of the equilibrium mixture is reduced at constant temperature.
(c) The equilibrium mixture is cooled.
(d) Gaseous argon (which does not react) is added to the equilibrium mixture while both the total gas pressure and the temperature are kept constant.
(e) Gaseous argon is added to the equilibrium mixture without changing the volume.

54. Explain the effect of each of the following stresses on the position of the equilibrium

$$SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}\,O_2(g)$$

The reaction as written is endothermic.

(a) $O_2(g)$ is added to the equilibrium mixture without changing volume or temperature.
(b) The mixture is compressed at constant temperature.
(c) The equilibrium mixture is cooled.
(d) An inert gas is pumped into the equilibrium mixture while the total gas pressure and the temperature are kept constant.
(e) An inert gas is added to the equilibrium mixture without changing the volume.

55. In a gas-phase reaction, it is observed that the equilibrium yield of products is increased by lowering the temperature and by reducing the volume.

(a) Is the reaction exothermic or endothermic?
(b) Is there a net increase or a net decrease in the number of gas molecules in the reaction?

56. The equilibrium constant of a gas-phase reaction increases as temperature is increased. When the nonreacting gas neon is admitted to a mixture of reacting gases (holding the temperature and the total pressure fixed and increasing the volume of the reaction vessel), the product yield is observed to decrease.

(a) Is the reaction exothermic or endothermic?
(b) Is there a net increase or a net decrease in the number of gas molecules in the reaction?

57. The most extensively used organic compound in the chemical industry is ethylene (C_2H_4). The two equations

$$C_2H_4(g) + Cl_2(g) \rightleftharpoons C_2H_4Cl_2(g)$$
$$C_2H_4Cl_2(g) \rightleftharpoons C_2H_3Cl(g) + HCl(g)$$

represent the way in which vinyl chloride (C_2H_3Cl) is synthesized for eventual use in polymeric plastics (polyvinyl chloride, PVC). The byproduct of the reaction, HCl, is now most cheaply made by this and similar reactions, rather than by direct combination of H_2 and Cl_2. Heat is given off in the first reaction and taken up in the second. Describe how you would design an industrial process to maximize the yield of vinyl chloride.

58. Methanol is made via the exothermic reaction

$$CO(g) + 2\,H_2(g) \longrightarrow CH_3OH(g)$$

Describe how you would control the temperature and pressure to maximize the yield of methanol.

The Direction of Change in Chemical Reactions: Thermodynamic Explanation

59. One way to manufacture ethanol is by the reaction

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$$

The ΔH_f° of $C_2H_4(g)$ is 52.3 kJ mol^{-1}; of $H_2O(g)$, −241.8 kJ mol^{-1}; and of $C_2H_5OH(g)$, −235.3 kJ mol^{-1}. Without doing detailed calculations, suggest the conditions of pressure and temperature that will maximize the yield of ethanol at equilibrium.

60. Dimethyl ether (CH_3OCH_3) is a good substitute for environmentally harmful propellants in aerosol spray cans. It is produced by the dehydration of methanol:

$$2\ CH_3OH(g) \rightleftharpoons CH_3OCH_3(g) + H_2O(g)$$

Describe reaction conditions that favor the equilibrium production of this valuable chemical. As a basis for your answer, compute ΔH° and ΔS° of the reaction from the data in Appendix D.

61. The equilibrium constant at 25°C for the reaction

$$2\ NO_2(g) \rightleftharpoons N_2O_4(g)$$

is 6.8. At 200°C the equilibrium constant is 1.21×10^{-3}. Calculate the enthalpy change (ΔH) for this reaction, assuming that ΔH and ΔS of the reaction are constant over the temperature range from 25°C to 200°C.

62. Stearic acid dimerizes when dissolved in hexane:

$$2\ C_{17}H_{35}COOH(hexane) \rightleftharpoons (C_{17}H_{35}COOH)_2(hexane)$$

The equilibrium constant for this reaction is 2900 at 28°C, but it drops to 40 at 48°C. Estimate ΔH° and ΔS° for the reaction.

63. The equilibrium constant for the reaction

$$\tfrac{1}{2}\ Cl_2(g) + \tfrac{1}{2}\ F_2(g) \rightleftharpoons ClF(g)$$

is measured to be 9.3×10^9 at 298 K and 3.3×10^7 at 398 K.

(a) Calculate ΔG° at 298 K for the reaction.

(b) Calculate ΔH° and ΔS°, assuming the enthalpy and entropy changes to be independent of temperature between 298 and 398 K.

64. Stearic acid also dimerizes when dissolved in carbon tetrachloride:

$$2\ C_{17}H_{35}COOH(CCl_4) \rightleftharpoons (C_{17}H_{35}COOH)_2(CCl_4)$$

The equilibrium constant for this reaction is 2780 at 22°C, but it drops to 93.1 at 42°C. Estimate ΔH° and ΔS° for the reaction.

65. For the synthesis of ammonia from its elements,

$$3\ H_2(g) + N_2(g) \rightleftharpoons 2\ NH_3(g)$$

the equilibrium constant $K = 5.9 \times 10^5$ at 298 K, and $\Delta H^\circ = -92.2$ kJ mol^{-1}. Calculate the equilibrium constant for the reaction at 600 K, assuming no change in ΔH° and ΔS° between 298 K and 600 K.

66. The cumulative exercise at the end of Chapter 14 explored reaction steps in the manufacture of sulfuric acid, including the oxidation of sulfur dioxide to sulfur trioxide:

$$SO_2(g) + \tfrac{1}{2}\ O_2(g) \rightleftharpoons SO_3(g)$$

At 25°C the equilibrium constant for this reaction is 2.6×10^{12}, but the reaction occurs very slowly. Calculate K for this reaction at 550°C, assuming ΔH° and ΔS° are independent of temperature in the range from 25°C to 550°C.

67. The vapor pressure of ammonia at −50°C is 0.4034 atm; at 0°C, it is 4.2380 atm.

(a) Calculate the molar enthalpy of vaporization (ΔH_{vap}) of ammonia.

(b) Calculate the normal boiling temperature of $NH_3(\ell)$.

68. The vapor pressure of butyl alcohol (C_4H_9OH) at 70.1°C is 0.1316 atm; at 100.8°C, it is 0.5263 atm.

(a) Calculate the molar enthalpy of vaporization (ΔH_{vap}) of butyl alcohol.

(b) Calculate the normal boiling point of butyl alcohol.

69. Although iodine is not very soluble in pure water, it dissolves readily in water that contains $I^-(aq)$ ion, thanks to the reaction

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

The equilibrium constant of this reaction was measured as a function of temperature with these results:

T:	3.8°C	15.3°C	25.0°C	35.0°C	50.2°C
K:	1160	841	689	533	409

(a) Plot ln K on the y axis as a function of $1/T$, the reciprocal of the absolute temperature.

(b) Estimate the ΔH° of this reaction.

70. Barium nitride vaporizes slightly at high temperature as it undergoes the dissociation

$$Ba_3N_2(s) \rightleftharpoons 3\ Ba(g) + N_2(g)$$

At 1000 K the equilibrium constant is 4.5×10^{-19}. At 1200 K the equilibrium constant is 6.2×10^{-12}.

(a) Estimate ΔH° for this reaction.

(b) The equation is rewritten as

$$2\ Ba_3N_2(s) \rightleftharpoons 6\ Ba(g) + 2\ N_2(g)$$

Now the equilibrium constant is 2.0×10^{-37} at 1000 K and 3.8×10^{-23} at 1200 K. Estimate ΔH° of *this* reaction.

Distribution of a Single Species between Immiscible Phases: Extraction and Separation Processes

71. An aqueous solution, initially 1.00×10^{-2} M in iodine (I_2), is shaken with an equal volume of an immiscible organic solvent, CCl_4. The iodine distributes itself between the aqueous and CCl_4 layers, and when equilibrium is reached at 27°C, the concentration of I_2 in the aqueous layer is 1.30×10^{-4} M. Calculate the partition coefficient K at 27°C for the reaction

$$I_2(aq) \rightleftharpoons I_2(CCl_4)$$

72. An aqueous solution, initially 2.50×10^{-2} M in iodine (I_2), is shaken with an equal volume of an immiscible organic solvent, CS_2. The iodine distributes itself between the aqueous and CS_2 layers, and when equilibrium is reached at 25°C, the concentration of I_2 in the aqueous layer is 4.16×10^{-5} M. Calculate the partition coefficient K at 25°C for the reaction

$$I_2(aq) \rightleftharpoons I_2(CS_2)$$

73. Benzoic acid (C_6H_5COOH) dissolves in water to the extent of 2.00 g L^{-1} at 15°C and in diethyl ether to the extent of 6.6×10^2 g L^{-1} at the same temperature.

(a) Calculate the equilibrium constants at 15°C for the two reactions

$$C_6H_5COOH(s) \rightleftharpoons C_6H_5COOH(aq)$$

and

$$C_6H_5COOH(s) \rightleftharpoons C_6H_5COOH(ether)$$

(b) From your answers to part (a), calculate the partition coefficient K for the reaction

$$C_6H_5COOH(aq) \rightleftharpoons C_6H_5COOH(ether)$$

74. Citric acid ($C_6H_8O_7$) dissolves in water to the extent of 1300 g L^{-1} at 15°C and in diethyl ether to the extent of 22 g L^{-1} at the same temperature.

(a) Calculate the equilibrium constants at 15°C for the two reactions

$$C_6H_8O_7(s) \rightleftharpoons C_6H_8O_7(aq)$$

and

$$C_6H_8O_7(s) \rightleftharpoons C_6H_8O_7(ether)$$

(b) From your answers to part (a), calculate the partition coefficient K for the reaction

$$C_6H_8O_7(aq) \rightleftharpoons C_6H_8O_7(ether)$$

ADDITIONAL PROBLEMS

75. At 298 K, unequal amounts of $BCl_3(g)$ and $BF_3(g)$ were mixed in a container. The gases reacted to form $BFCl_2(g)$ and $BClF_2(g)$. When equilibrium was finally reached, the four gases were present in these relative chemical amounts: BCl_3(90), BF_3(470), $BClF_2$(200), $BFCl_2$(45).

(a) Determine the equilibrium constants at 298 K of the two reactions

$$2\ BCl_3(g) + BF_3(g) \rightleftharpoons 3\ BFCl_2(g)$$

$$BCl_3(g) + 2\ BF_3(g) \rightleftharpoons 3\ BClF_2(g)$$

(b) Determine the equilibrium constant of the reaction

$$BCl_3(g) + BF_3(g) \rightleftharpoons BFCl_2 + BClF_2(g)$$

and explain why knowing this equilibrium constant really adds nothing to what you knew in part (a).

76. Methanol can be synthesized by means of the equilibrium reaction

$$CO(g) + 2\ H_2(g) \rightleftharpoons CH_3OH(g)$$

for which the equilibrium constant at 225°C is 6.08×10^{-3}. Assume that the ratio of the pressures of $CO(g)$ and $H_2(g)$ is 1:2. What values should they have if the partial pressure of methanol is to be 0.500 atm?

77. At equilibrium at 425.6°C, a sample of *cis*-1-methyl-2-ethylcyclopropane is 73.6% converted into the *trans* form:

$$cis \rightleftharpoons trans$$

(a) Compute the equilibrium constant K for this reaction.

(b) Suppose that 0.525 mol of the *cis* compound is placed in a 15.00-L vessel and heated to 425.6°C. Compute the equilibrium partial pressure of the *trans* compound.

78. The equilibrium constant for the reaction

$$(CH_3)_3COH(g) \rightleftharpoons (CH_3)_2CCH_2(g) + H_2O(g)$$

is 2.42 at 450 K.

(a) A pure sample of the reactant, which is named "*t*-butanol," is confined in a container of fixed volume at a temperature of 450 K and at an original pressure of 0.100 atm. Calculate the fraction of this starting material that is converted to products at equilibrium.

(b) A second sample of the reactant is confined, this time at an original pressure of 5.00 atm. Again, calculate the fraction of the starting material that is converted to products at equilibrium.

79. At 627°C and 1 atm, SO_3 is partly dissociated into SO_2 and O_2:

$$SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}\ O_2(g)$$

The density of the equilibrium mixture is 0.925 g L^{-1}. What is the degree of dissociation of SO_3 under these circumstances?

80. Acetic acid in the vapor phase consists of both monomeric and dimeric forms in equilibrium:

$$2\ CH_3COOH(g) \rightleftharpoons (CH_3COOH)_2(g)$$

At 110°C the equilibrium constant for this reaction is 3.72.

(a) Calculate the partial pressure of the dimer when the total pressure is 0.725 atm at equilibrium.

(b) What percentage of the acetic acid is dimerized under these conditions?

* **81.** Repeat the calculation of problem 36 with a total pressure of 100 atm. (*Note:* Here it is necessary to solve the equation by successive approximations. See Appendix C.)

82. At 900 K the equilibrium constant for the reaction

$$\tfrac{1}{2}\ O_2(g) + SO_2(g) \rightleftharpoons SO_3(g)$$

has the value $K = 0.587$. What will be the equilibrium partial pressure of $O_2(g)$ if a sample of SO_3 weighing 0.800 g is heated to 900 K in a quartz-glass vessel whose volume is 100.0 cm^3? (*Note:* Here it is necessary to solve the equation by successive approximations. See Appendix C.)

* **83.** At 298 K chlorine is only slightly soluble in water. Thus, under a pressure of 1.00 atm of $Cl_2(g)$, 1.00 L of water at equilibrium dissolves just 0.091 mol of Cl_2.

$$Cl_2(g) \rightleftharpoons Cl_2(aq)$$

In such solutions the $Cl_2(aq)$ concentration is 0.061 M and the concentrations of $Cl^-(aq)$ and $HOCl(aq)$ are both 0.030 M. These two additional species are formed by the equilibrium

$$Cl_2(aq) + H_2O(\ell) \rightleftharpoons H^+(aq) + Cl^-(aq) + HOCl(aq)$$

There are no other Cl-containing species. Compute the equilibrium constants K_1 and K_2 for the two reactions.

84. At 400°C the reaction

$$BaO_2(s) + 4\ HCl(g) \rightleftarrows BaCl_2(s) + 2\ H_2O(g) + Cl_2(g)$$

has an equilibrium constant equal to K_1. How is K_1 related to the equilibrium constant K_2 of the reaction

$$2\ Cl_2(g) + 4\ H_2O(g) + 2\ BaCl_2(s) \rightleftarrows 8\ HCl(g) + 2\ BaO_2(s)$$

at 400°C?

85. Ammonium hydrogen sulfide, a solid, decomposes to give $NH_3(g)$ and $H_2S(g)$. At 25°C, some $NH_4HS(s)$ is placed in an evacuated container. A portion of it decomposes, and the total pressure at equilibrium is 0.659 atm. Extra $NH_3(g)$ is then injected into the container, and when equilibrium is reestablished, the partial pressure of $NH_3(g)$ is 0.750 atm.

(a) Compute the equilibrium constant for the decomposition of ammonium hydrogen sulfide.

(b) Determine the final partial pressure of $H_2S(g)$ in the container.

86. The equilibrium constant for the reaction

$$KOH(s) + CO_2(g) \rightleftarrows KHCO_3(s)$$

is 6×10^{15} at 25°C. Suppose 7.32 g of KOH and 9.41 g of $KHCO_3$ are placed in a closed evacuated container and allowed to reach equilibrium. Calculate the pressure of $CO_2(g)$ at equilibrium.

87. The equilibrium constant for the reduction of nickel(II) oxide to nickel at 754°C is 255.4, corresponding to the reaction

$$NiO(s) + CO(g) \rightleftarrows Ni(s) + CO_2(g)$$

If the total pressure of the system at 754°C is 2.50 atm, calculate the partial pressures of $CO(g)$ and $CO_2(g)$.

88. Both glucose (corn sugar) and fructose (fruit sugar) taste sweet, but fructose tastes sweeter. Each year in the United States, tons of corn syrup destined to sweeten food are treated to convert glucose as fully as possible to the sweeter fructose. The reaction is an equilibrium:

$$\text{glucose} \rightleftarrows \text{fructose}$$

(a) A 0.2564 M solution of pure glucose is treated at 25°C with an enzyme (catalyst) that causes the preceding equilibrium to be reached quickly. The final concentration of fructose is 0.1175 M. In another experiment at the same temperature, a 0.2666 M solution of pure fructose is treated with the same enzyme and the final concentration of glucose is 0.1415 M. Compute an average equilibrium constant for the preceding reaction.

(b) At equilibrium under these conditions, what percentage of glucose is converted to fructose?

89. At 300°C the equilibrium constant for the reaction

$$PCl_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$$

is $K = 11.5$.

(a) Calculate the reaction quotient Q if initially $P_{PCl_3} = 2.0$ atm, $P_{Cl_2} = 6.0$ atm, and $P_{PCl_5} = 0.10$ atm. State whether the reaction proceeds to the right or to the left as equilibrium is approached.

(b) Calculate P_{PCl_3}, P_{Cl_2}, and P_{PCl_5} at equilibrium.

(c) If the volume of the system is then increased, will the amount of PCl_5 present increase or decrease?

90. Although the process of dissolution of helium gas in water is favored in terms of energy, helium is only very slightly soluble in water. What keeps this gas from dissolving in great quantities in water?

91. The hydrogenation of pyridine to piperidine

$$C_5H_5N(g) + 3\ H_2(g) \rightleftarrows C_5H_{11}N(g)$$

is an equilibrium process whose equilibrium constant is given by the equation

$$\log_{10} K = -20.281 + \frac{10.560\ \text{K}}{T}$$

(a) Calculate the value of K at $T = 500$ K.

(b) If the partial pressure of hydrogen is 1.00 atm, what fraction of the nitrogen is in the form of pyridine molecules at $T = 500$ K?

92. The breaking of the O—O bond in peroxydisulfuryl difluoride (FO_2SOOSO_2F) gives FO_2SO:

$$(FO_2SO)_2 \rightleftarrows 2\ FO_2SO$$

The compound on the left of this equation is a colorless liquid that boils at 67.1°C. Its vapor, when heated to about 100°C, turns brown as the product of the reaction forms. Suppose that, in a sample of the vapor, the intensity of the brown color doubles between 100°C and 110°C and that the total pressure increases only by the 2.7% predicted for an ideal gas. Estimate $\Delta H°$ for the preceding reaction.

93. Polychlorinated biphenyls (PCBs) are a major environmental problem. These oily substances have many uses, but they resist breakdown by bacterial action when spilled in the environment and, being fat-soluble, can accumulate to dangerous concentrations in the fatty tissues of fish and animals. One little-appreciated complication in controlling the problem is that there are *209* different PCBs, all now in the environment. They are generally similar, but their solubilities in fats differ considerably. The best measure of this is K_{ow}, the equilibrium constant for the partition of a PCB between the fat-like solvent octanol and water.

$$\text{PCB}(aq) \rightleftarrows \text{PCB}(octanol)$$

An equimolar mixture of PCB-2 and PCB-11 in water is treated with an equal volume of octanol. Determine the ratio between the amounts of PCB-2 and PCB-11 in the water at equilibrium. At room temperature, K_{ow} is 3.98×10^4 for PCB-2 and 1.26×10^5 for PCB-11.

94. Refer to the data in problems 73 and 74. Suppose 2.00 g of a solid consisting of 50.0% benzoic acid and 50.0% citric acid by mass is added to 100.0 mL of water and 100.0 mL of diethyl ether and the whole assemblage is shaken. When the immiscible layers are separated and the solvents are removed by evaporation, two solids result. Calculate the percentage (by mass) of the major component in each solid.

95. At 25°C the partition coefficient for the equilibrium

$$I_2(aq) \rightleftarrows I_2(CCl_4)$$

has the value $K = 85$. To 0.100 L of an aqueous solution, which is initially 2×10^{-3} M in I_2, we add 0.025 L of CCl_4. The mixture is shaken in a separatory funnel and allowed to separate into two phases, and the CCl_4 phase is withdrawn.

(a) Calculate the fraction of the I_2 remaining in the aqueous phase.

(b) Suppose the remaining aqueous phase is shaken with another 0.025 L of CCl_4 and again separated. What fraction of the I_2 from the original aqueous solution is *now* in the aqueous phase?

(c) Compare your answer with that of Example 9.18, in which the same total amount of CCl_4 (0.050 L) was used in a *single* extraction. For a given total amount of extracting solvent, which is the more efficient way to remove iodine from water?

96. From the data in Appendix D calculate $\Delta H°$, $\Delta G°$, and K, for the following reaction at 298 K:

$$6\ CH_4(g) + \tfrac{9}{2}\ O_2(g) \longrightarrow C_6H_6(\ell) + 9\ H_2O(\ell)$$

CUMULATIVE PROBLEMS

97. The reaction

$$P_4(g) \rightleftharpoons 2\ P_2(g)$$

is endothermic and begins to occur at moderate temperatures.

(a) In which direction do you expect deviations to occur from Boyle's law, $P \propto 1/V$ (constant T), for gaseous P_4?

(b) In which direction do you expect deviations to occur from Charles's law, $V \propto T$ (constant P), for gaseous P_4?

98. A 4.72-g mass of methanol, CH_3OH, is placed in an evacuated 1.00-L flask and heated to 250°C. It vaporizes and then reaches the following equilibrium:

$$CH_3OH(g) \rightleftharpoons CO(g) + 2\ H_2(g)$$

A tiny hole forms in the side of the container, allowing a small amount of gas to effuse out. Analysis of the escaping gases shows that the rate of escape of the hydrogen is 33 times the rate of escape of the methanol. Calculate the equilibrium constant for the preceding reaction at 250°C.

99. The triple bond in the N_2 molecule is very strong, but at high enough temperatures even it breaks down. At 5000 K, when the total pressure exerted by a sample of nitrogen is 1.00 atm, $N_2(g)$ is 0.65% dissociated at equilibrium:

$$N_2(g) \rightleftharpoons 2\ N(g)$$

At 6000 K with the same total pressure, the proportion of $N_2(g)$ dissociated at equilibrium rises to 11.6%. Use the van't Hoff equation to estimate the ΔH of this reaction.

100. At 25°C the equilibrium constant for the reaction

$$CaSO_4(s) + 2\ H_2O(g) \rightleftharpoons CaSO_4{\cdot}2H_2O(s)$$

is 1.6×10^3. Over what range of relative humidities do you expect $CaSO_4(s)$ to be converted to $CaSO_4{\cdot}2H_2O$? (*Note:* The relative humidity is the partial pressure of water vapor divided by its equilibrium vapor pressure and multiplied by 100%. Use Table 10.1.)

101. Calculate the equilibrium pressure (in atmospheres) of $O_2(g)$ over a sample of pure $NiO(s)$ in contact with pure $Ni(s)$ at 25°C. The $NiO(s)$ decomposes according to the equation

$$NiO(s) \longrightarrow Ni(s) + \tfrac{1}{2}\ O_2(g)$$

Use data from Appendix D.

102. **(a)** From the values in Appendix D, find the enthalpy change and the Gibbs free energy change when one mole of benzene C_6H_6 is vaporized at 25°C.

(b) Calculate the vapor pressure of benzene at 25°C.

(c) Assuming that the enthalpy and entropy of vaporization are constant, estimate the normal boiling point of benzene.

103. Snow and ice sublime spontaneously when the partial pressure of water vapor is below the equilibrium vapor pressure of ice. At 0°C the vapor pressure of ice is 0.0060 atm (the triple-point pressure of water). Taking the enthalpy of sublimation of ice to be 50.0 kJ mol^{-1}, calculate the partial pressure of water vapor below which ice will sublime spontaneously at −15°C.

104. The sublimation pressure of solid NbI_5 is the pressure of gaseous NbI_5 present in equilibrium with the solid. It is given by the empirical equation

$$\log P = -6762/T + 8.566$$

The vapor pressure of liquid NbI_5, on the other hand, is given by

$$\log P = -4653/T + 5.43$$

In these two equations, T is the absolute temperature in kelvins and P is the pressure in atmospheres.

(a) Determine the enthalpy and entropy of sublimation of $NbI_5(s)$.

(b) Determine the enthalpy and entropy of vaporization of $NbI_5(\ell)$.

(c) Calculate the normal boiling point of $NbI_5(\ell)$.

(d) Calculate the triple-point temperature and pressure of NbI_5. (*Hint:* At the triple point of a substance, the liquid and solid are in equilibrium and must have the same vapor pressure. If they did not, vapor would continually escape from the phase with the higher vapor pressure and collect in the phase with the lower vapor pressure.)

105. In an extraction process, a solute species is partitioned between two immiscible solvents. Suppose the two solvents are water and carbon tetrachloride. State which phase will have the higher concentration of each of the following solutes: (a) CH_3OH, (b) C_2Cl_6, (c) Br_2, (d) NaCl. Explain your reasoning.

106. The gaseous compounds allene and propyne are isomers with formula C_3H_4. Calculate the equilibrium constant and the standard enthalpy change at 25°C for the isomerization reaction

$$\text{allene}(g) \rightleftharpoons \text{propyne}(g)$$

from the following data, all of which apply to 298 K:

	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})
Allene	192	202
Propyne	185	194

107. (a) Calculate the standard free-energy change and the equilibrium constant for the dimerization of NO_2 to N_2O_4 at 25°C (see Appendix D).

(b) Calculate ΔG for this reaction at 25°C when the pressures of NO_2 and N_2O_4 are each held at 0.010 atm. Which way will the reaction tend to proceed?

108. There are two isomeric hydrocarbons with formula C_4H_{10}, butane and isobutane, which we denote here B and I. The standard enthalpies of formation for the gaseous species are -124.7 kJ mol^{-1} for B, -131.3 kJ mol^{-1} for I; the standard free energies of formation are -15.9 kJ mol^{-1} for B, -18.0 kJ mol^{-1} for I.

(a) Which is the more stable under standard conditions, and which has the higher entropy?

(b) The reaction $B \rightleftharpoons I$ can occur in the presence of a catalyst. Calculate the equilibrium constant at 298 K for the conversion of B to I, and calculate the percentage of B in the equilibrium mixture.

109. At 3500 K the equilibrium constant for the reaction $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$ is 8.28.

(a) What is $\Delta G^\circ(3500)$ for this reaction?

(b) What is ΔG at 3500 K for transforming 1 mol CO_2 and 1 mol H_2, both held at 0.1 atm, to 1 mol CO and 1 mol H_2O, both held at 2 atm?

(c) In which direction would this last reaction run spontaneously?

110. At 1200 K in the presence of solid carbon, an equilibrium mixture of CO and CO_2 (called "producer gas") contains 98.3 mol percent CO and 1.69 mol percent of CO_2 when the total pressure is 1 atm. The reaction is

$$CO_2(g) + C(\textit{graphite}) \rightleftharpoons 2\ CO(g)$$

(a) Calculate P_{CO} and P_{CO_2}.

(b) Calculate the equilibrium constant.

(c) Calculate ΔG° for this reaction.

111. (a) Formulate the equilibrium expression for the endothermic reaction

$$AgCl{\cdot}NH_3(s) \rightleftharpoons AgCl(s) + NH_3(g)$$

(b) What is the effect on P_{NH_3} at equilibrium if additional $AgCl(s)$ is added?

(c) What is the effect on P_{NH_3} at equilibrium if additional $NH_3(g)$ is pumped into or out of the system, provided that neither of the two solid phases shown in the chemical equation is completely used up?

(d) What is the effect on P_{NH_3} of lowering the temperature?

112. Solid ammonium carbonate decomposes according to the equation

$$(NH_4)_2CO_3(s) \rightleftharpoons 2\ NH_3(g) + CO_2(g) + H_2O(g)$$

At a certain elevated temperature the total pressure of the gases NH_3, CO_2, and H_2O generated by the decomposition of, and at equilibrium with, pure solid ammonium carbonate is 0.400 atm. Calculate the equilibrium constant for the reaction considered. What would happen to P_{NH_3} and P_{CO_2} if P_{H_2O} were adjusted by external means to be 0.200 atm without changing the relative amounts of $NH_3(g)$ and $CO_2(g)$ and with $(NH_4)_2CO_3(s)$ still being present?

CHAPTER 15

Acid–Base Equilibria

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Many naturally occurring dyes change color as the acidity of their surroundings changes. The compound cyanidin is blue in the basic sap of the cornflower and red in the acidic sap of the poppy. Such dyes can be used as indicators of the degree of acidity in a medium.

According to Chapter 11, an acid is a substance that upon dissolving in water increases the concentration of hydronium (H_3O^+) ions above the value found in pure water, and a base is a substance that increases the concentration of hydroxide (OH^-) ions above its value in pure water. Despite the careful language, it is commonplace to view acids and bases as substances that dissociate to give protons (which upon hydration become hydronium ions) and hydroxide ions, respectively. If the dissociation is complete, we can easily calculate the concentration of hydronium and hydroxide ions in the solution and then calculate the yield of acid–base neutralization reactions, and acid–base titrations, by the methods of stoichiometry in solution. But experience shows that many acid–base reactions do not go to completion. So, to predict the amount (or concentration) of their products, we have to use the ideas and methods of chemical equilibrium developed in Chapter 14. The present chapter deals with a fundamental aspect of acid–base chemistry key to its applications in the physical and biological sciences, in engineering, and in medicine: How far do such reactions proceed before reaching equilibrium?

Although many acid–base reactions occur in the gaseous and solid states and in nonaqueous solutions, this chapter focuses on acid–base reactions in aqueous solutions. Such solutions play important roles in everyday life. Vinegar, orange juice, and battery fluid are familiar acidic aqueous solutions. Basic solutions are produced when such common products as borax, baking soda, and antacids are dissolved in water. Acid–base chemistry will appear many times throughout the rest of this book. We consider the effects of acidity on the dissolution of solids in Chapter 16, on redox reactions in electrochemical cells in Chapter 17, and on the rates of reaction in Chapter 18. At the end of this chapter we relate acid strength to molecular structure in organic acids, and in Chapter 23 we point out the central roles of amino acids and nucleic acids in biochemistry. The reactions of acids and bases lie at the heart of nearly all branches of chemistry.

15.1 Classifications of Acids and Bases

In Section 11.3 we introduced acids and bases, as defined by Arrhenius. An **acid** is a substance that when dissolved in water increases the concentration of hydronium ion (H_3O^+) above the value it takes in pure water. A **base** increases the concentration of hydroxide ion (OH^-). In preparation for discussing acid–base equilibria we want to generalize these definitions to accommodate broader classes of compounds that are chemically similar to the familiar acids and bases. The first of these more general definitions was introduced by Brønsted and Lowry and the second by Lewis.

Brønsted–Lowry Acids and Bases

A broader definition of acids and bases, which will be useful in quantitative calculations in this chapter, was proposed independently by Johannes Brønsted and Thomas Lowry in 1923. A **Brønsted–Lowry acid** is defined as a substance that can *donate* a hydrogen ion, and a **Brønsted–Lowry base** is a substance that can *accept* a hydrogen ion. In a Brønsted–Lowry acid–base reaction, hydrogen ions are transferred from the acid to the base. When acetic acid is dissolved in water,

$$\underset{\text{Acid}_1}{CH_3COOH(aq)} + \underset{\text{Base}_2}{H_2O(\ell)} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+(aq)} + \underset{\text{Base}_1}{CH_3COO^-(aq)}$$

hydrogen ions are transferred from acetic acid to water. Throughout this chapter, the hydronium ion, $H_3O^+(aq)$, rather than $H^+(aq)$, will be used to represent the true nature of hydrogen ions in water (Fig. 15.1). Acids and bases occur as **conjugate acid–base pairs.** CH_3COOH and CH_3COO^- form such a pair, where CH_3COO^- is the conjugate base of CH_3COOH (equivalently, CH_3COOH is the conjugate acid of CH_3COO^-). In the same way, H_3O^+ and H_2O form a conjugate acid–base pair. The equilibrium that is established may be pictured as the competition between two bases for hydrogen ions. When ammonia is dissolved in water,

$$\underset{\text{Acid}_1}{H_2O(\ell)} + \underset{\text{Base}_2}{NH_3(aq)} \rightleftharpoons \underset{\text{Acid}_2}{NH_4^+(aq)} + \underset{\text{Base}_1}{OH^-(aq)}$$

the two bases NH_3 and OH^- compete for hydrogen ions.

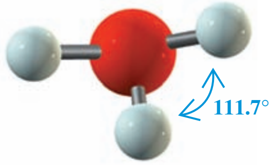


FIGURE 15.1 The structure of the hydronium ion (H_3O^+).

The Brønsted–Lowry definition has the advantage of not being limited to aqueous solutions. An example with liquid ammonia as the solvent is

$$\underset{\text{Acid}_1}{\text{HCl(in NH}_3)} + \underset{\text{Base}_2}{\text{NH}_3(\ell)} \rightleftharpoons \underset{\text{Acid}_2}{\text{NH}_4^+\text{(in NH}_3)} + \underset{\text{Base}_1}{\text{Cl}^-\text{(in NH}_3)}$$

The NH_3 acts as a base even though hydroxide ion, OH^-, is not present.

Some molecules and ions function either as acids or bases depending on reaction conditions and are called **amphoteric.** The most common example is water itself. Water acts as an acid in donating a hydrogen ion to NH_3 (its conjugate base here is OH^-) and as a base in accepting a hydrogen ion from CH_3COOH (its conjugate acid here is H_3O^+). In the same way, the hydrogen carbonate ion can act as an acid

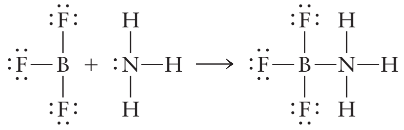
$$\text{HCO}_3^-(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CO}_3^{2-}(aq)$$

or as a base:

$$\text{HCO}_3^-(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{CO}_3(aq) + \text{OH}^-(aq)$$

Lewis Acids and Bases

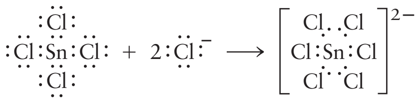
The Lewis bonding model with its electron pairs can be used to define a more general kind of acid–base behavior of which the Arrhenius and Brønsted–Lowry definitions are special cases. A **Lewis base** is any species that donates lone-pair electrons, and a **Lewis acid** is any species that accepts such electron pairs. The Arrhenius acids and bases considered so far fit this description (with the Lewis acid, H^+, acting as an acceptor toward various Lewis bases such as NH_3 and OH^-, the electron pair donors). Other reactions that do *not* involve hydrogen ions can still be considered Lewis acid–base reactions. An example is the reaction between electron-deficient BF_3 and electron-rich NH_3:



Here ammonia, the Lewis base, donates lone-pair electrons to BF_3, the Lewis acid or electron acceptor. The bond that forms is called a **coordinate covalent bond,** in which both electrons are supplied by a lone pair on the Lewis base.

Octet-deficient compounds involving elements of Group III, such as boron and aluminum, are often strong Lewis acids because Group III atoms can achieve octet configurations by forming coordinate covalent bonds. Atoms and ions from Groups V through VII have the necessary lone pairs to act as Lewis bases. Compounds of main-group elements from the later periods can also act as Lewis acids through valence expansion. In such reactions the central atom accepts a share in additional lone pairs beyond the eight electrons needed to satisfy the octet rule. For example, $SnCl_4$ is a Lewis acid that accepts electrons from chloride ion lone pairs:

$$\text{SnCl}_4(\ell) + 2\ \text{Cl}^-(aq) \longrightarrow [\text{SnCl}_6]^{2-}(aq)$$



After the reaction, each tin atom is surrounded by 12 rather than 8 valence electrons.

The Lewis definition systematizes the chemistry of a great many binary oxides, which can be considered as anhydrides of acids or bases. An **acid anhydride** is obtained by removing water from an oxoacid (see Section 11.3) until only the oxide remains; thus, CO_2 is the anhydride of carbonic acid (H_2CO_3).

EXAMPLE 15.1

What is the acid anhydride of phosphoric acid (H_3PO_4)?

SOLUTION

If the formula unit H_3PO_4 (which contains an odd number of hydrogen atoms) is doubled, $H_6P_2O_8$ is obtained. Subtraction of 3 H_2O from this gives P_2O_5, which is the empirical formula of tetraphosphorus decaoxide (P_4O_{10}). This compound is the acid anhydride of phosphoric acid.

Related Problems: 9, 10

The Lewis definition provides a way to organize the chemistry of the main group oxides. The oxides of most of the nonmetals are **acid anhydrides,** which react with an excess of water to form acidic solutions. Examples are

$$N_2O_5(s) + H_2O(\ell) \longrightarrow 2\ HNO_3(aq) \longrightarrow 2\ H^+(aq) + 2\ NO_3^-(aq)$$

$$SO_3(g) + H_2O(\ell) \longrightarrow H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq)$$

Silica (SiO_2) is the acid anhydride of the very weak silicic acid H_2SiO_3, a gelatinous material that is insoluble in water but readily dissolves in strongly basic aqueous solutions according to

$$H_2SiO_3(s) + 2\ OH^-(aq) \longrightarrow SiO_3^{2-}(aq) + 2\ H_2O(\ell)$$

Oxides of Group I and II metals are **base anhydrides,** obtained by removing water from the corresponding hydroxides. Calcium oxide, CaO, is the base anhydride of calcium hydroxide, $Ca(OH)_2$. The removal of water from $Ca(OH)_2$ is the reverse of the addition of water to the oxide:

$$CaO(s) + H_2O(\ell) \longrightarrow Ca(OH)_2(s)$$

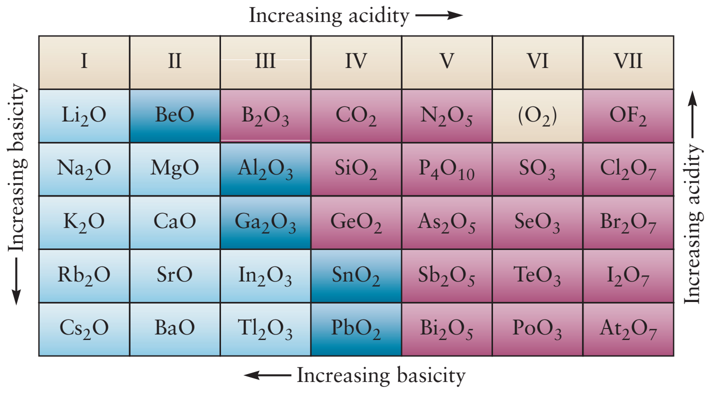
$$Ca(OH)_2(s) \longrightarrow CaO(s) + H_2O(\ell)$$

The base anhydride of NaOH is Na_2O. Oxides of metals in the middle groups of the periodic table (III through V) lie on the border between ionic and covalent behavior and are frequently amphoteric. An example is aluminum oxide (Al_2O_3), which dissolves to only a limited extent in water but much more readily in either acids or bases:

Acting as a base: $Al_2O_3(s) + 6\ H_3O^+(aq) \longrightarrow 2\ Al^{3+}(aq) + 9\ H_2O(\ell)$

Acting as an acid: $Al_2O_3(s) + 2\ OH^-(aq) + 3\ H_2O(\ell) \longrightarrow 2\ Al(OH)_4^-(aq)$

Figure 15.2 summarizes the acid–base character of the main-group oxides in the first periods.



I	II	III	IV	V	VI	VII
Li_2O	BeO	B_2O_3	CO_2	N_2O_5	(O_2)	OF_2
Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
K_2O	CaO	Ga_2O_3	GeO_2	As_2O_5	SeO_3	Br_2O_7
Rb_2O	SrO	In_2O_3	SnO_2	Sb_2O_5	TeO_3	I_2O_7
Cs_2O	BaO	Tl_2O_3	PbO_2	Bi_2O_5	PoO_3	At_2O_7

FIGURE 15.2 Among the oxides of the main-group elements, acidity tends to increase from left to right and from bottom to top in the periodic table. Oxygen difluoride is only weakly acidic. Oxides shown in light blue are derived from metals, those in dark blue from metalloids, and those in dark red from nonmetals.

Although oxoacids and hydroxides are Arrhenius acids and bases (they release $H_3O^+(aq)$ or $OH^-(aq)$ into aqueous solution), acid and base anhydrides do not fall into this classification because they contain neither H^+ nor OH^-. Acid anhydrides are acids in the Lewis sense, (they accept electron pairs), and base anhydrides are bases in the Lewis sense, (their O^{2-} ions donate electron pairs). The reaction between an acid anhydride and a base anhydride is then a Lewis acid–base reaction. An example of such a reaction is

$$\mathrm{CaO}(s) + \mathrm{CO_2}(g) \longrightarrow \mathrm{CaCO_3}(s)$$

Here, the Lewis base CaO donates an electron pair (one of the lone pairs of the oxygen atom) to the Lewis acid (CO_2) to form a coordinate covalent bond in the CO_3^{2-} ion. Similar Lewis acid–base reactions can be written for other acid–base anhydride pairs. Sulfur trioxide, for example, reacts with metal oxides to form sulfates:

$$\mathrm{MgO}(s) + \mathrm{SO_3}(g) \longrightarrow \mathrm{MgSO_4}(s)$$

Note that these reactions are not redox reactions (oxidation numbers do not change). They are clearly not dissolution or precipitation reactions, nor are they acid–base reactions in the Arrhenius sense. But they are usefully classified as acid–base reactions in the Lewis sense.

Comparison of Arrhenius, Brønsted–Lowry, and Lewis Definitions

The neutralization reaction between HCl and NaOH

$$\underset{\text{Acid}}{\mathrm{HCl}} + \underset{\text{Base}}{\mathrm{NaOH}} \longrightarrow \underset{\text{Water}}{\mathrm{H_2O}} + \underset{\text{Salt}}{\mathrm{NaCl}}$$

introduced in Section 11.3 shows the progressive generality in these definitions. By the Arrhenius definition, HCl is the acid and NaOH is the base. By the Brønsted–Lowry definition, H_3O^+ is the acid and OH^- is the base. According to Lewis, H^+ is the acid and OH^- the base, because the proton accepts the lone pair donated by OH^- in the reaction

$$\mathrm{H^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{H_2O}(\ell)$$

15.2 Properties of Acids and Bases in Aqueous Solutions: The Brønsted–Lowry Scheme

Chapters 10 and 11 describe the special properties of liquid water. Because of its substantial dipole moment, water is especially effective as a solvent, stabilizing both polar and ionic solutes. Water is not only the solvent, but also participates in acid–base reactions as a reactant. Water plays an integral role in virtually all biochemical reactions essential to the survival of living organisms; these reactions involve acids, bases, and ionic species. In view of the wide-ranging importance of these reactions, we devote the remainder of this chapter to acid–base behavior and related ionic reactions in aqueous solution. The Brønsted–Lowry definition of acids and bases is especially well suited to describe these reactions.

TABLE 15.1 Temperature Dependence of K_w

T(°C)	K_w	pH of Water
0	0.114×10^{-14}	7.47
10	0.292×10^{-14}	7.27
20	0.681×10^{-14}	7.08
25	1.01×10^{-14}	7.00
30	1.47×10^{-14}	6.92
40	2.92×10^{-14}	6.77
50	5.47×10^{-14}	6.63
60	9.61×10^{-14}	6.51

Autoionization of Water

What happens when water acts as both acid and base in the same reaction? The resulting equilibrium is

$$\underset{\text{Acid}_1}{H_2O(\ell)} + \underset{\text{Base}_2}{H_2O(\ell)} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+(aq)} + \underset{\text{Base}_1}{OH^-(aq)}$$

or

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

This reaction is responsible for the **autoionization** of water, which leads to small but measurable concentrations of hydronium and hydroxide ions at equilibrium. The equilibrium expression for this reaction is

$$[H_3O^+][OH^-] = K_w \qquad \textbf{[15.1]}$$

The equilibrium constant for this particular reaction has a special symbol: K_w, and a special name, the **ion product constant for water;** its value is 1.0×10^{-14} at 25°C. Because the liquid water appears in this equilibrium reaction equation as a pure substance, it is considered already to be in its reference state, and therefore contributes only the factor 1 to the mass action law equilibrium expression. The reasons for this are discussed more fully in Sections 14.2 and 14.3. The temperature dependence of K_w is given in Table 15.1; all problems in this chapter are assumed to refer to 25°C unless otherwise stated.

Pure water contains no ions other than H_3O^+ and OH^-, and to maintain overall electrical neutrality, an equal number of ions of each type must be present. Putting these facts into the equilibrium expression Equation 15.1 gives

$$[H_3O^+] = [OH^-] = y$$
$$y^2 = 1.0 \times 10^{-14}$$
$$y = 1.0 \times 10^{-7}$$

so that in pure water at 25°C the concentrations of both H_3O^+ and OH^- are 1.0×10^{-7} M.

Strong Acids and Bases

An aqueous acidic solution contains an excess of H_3O^+ over OH^- ions. A **strong acid** is one that ionizes almost completely in aqueous solution. When the strong acid HCl (hydrochloric acid) is put in water, the reaction

$$HCl(aq) + H_2O(\ell) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

occurs. A single rather than a double arrow indicates that the reaction is essentially complete. Another strong acid is perchloric acid ($HClO_4$). (See Table 11.1.) If 0.10 mol of either of these acids is dissolved in enough water to make 1.0 L of solution, 0.10 M concentration of $H_3O^+(aq)$ results. Because the acid–base properties of solutions are determined by their concentrations of $H_3O^+(aq)$, these two strong acids have the same effect in water despite differences we shall see shortly in their intrinsic abilities to donate hydrogen ions. Water is said to have a **leveling effect** on a certain group of acids (HCl, HBr, HI, H_2SO_4, HNO_3, and $HClO_4$) because they all behave as strong acids when water is the solvent. The reactions of these acids with water all lie so far to the right at equilibrium that the differences between the acids are negligible. The concentration of H_3O^+ in a 0.10 M solution of *any* strong acid that donates one hydrogen ion per molecule is simply 0.10 M. We use this result in Equation 15.1 to obtain the OH^- concentration

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13}\ \text{M}$$

In the same fashion, we define a **strong base** as one that reacts essentially completely to give $OH^-(aq)$ ion when put in water. The amide ion (NH_2^-) and the hydride ion (H^-) are both strong bases. For every mole per liter of either of these ions that is added to water, one mole per liter of $OH^-(aq)$ forms. Note that the other products in these reactions are gaseous NH_3 and H_2, respectively:

$$H_2O(\ell) + NH_2^-(aq) \longrightarrow NH_3(aq) + OH^-(aq)$$

$$H_2O(\ell) + H^-(aq) \longrightarrow H_2(aq) + OH^-(aq)$$

The important base sodium hydroxide, a solid, increases the OH^- concentration in water when it dissolves:

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$

For every mole of NaOH that dissolves in water, one mole of $OH^-(aq)$ forms, so NaOH is a strong base. Strong bases are leveled in aqueous solution in the same way that strong acids are leveled. If 0.10 mol of NaOH or NH_2^- or H^- is put into enough water to make 1.0 L of solution, then in every case

$$[OH^-] = 0.10 \text{ M}$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13} \text{ M}$$

The OH^- contribution from the autoionization of water is negligible here, as was the contribution of H_3O^+ from autoionization in the 0.10 M HCl and $HClO_4$ solutions. When only a very small amount of strong acid or base is added to pure water (for example, 10^{-7} mol L^{-1}), we have to include the autoionization of water to describe the concentration of hydronium and hydroxide ions accurately.

The pH Function

In aqueous solution the concentration of hydronium ion can range from 10 M to 10^{-15} M. It is convenient to compress this enormous range by introducing a logarithmic acidity scale, called **pH** and defined by

$$pH = -\log_{10} [H_3O^+] \qquad [15.2]$$

Pure water at 25°C has $[H_3O^+] = 1.0 \times 10^{-7}$ M, so

$$pH = -\log_{10} (1.0 \times 10^{-7}) = -(-7.00) = 7.00$$

A 0.10 M solution of HCl has $[H_3O^+] = 0.10$ M, so

$$pH = -\log_{10} (0.10) = -\log_{10} (1.0 \times 10^{-1}) = -(-1.00) = 1.00$$

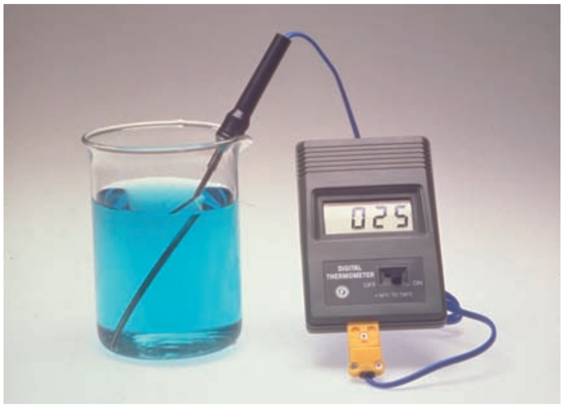
and at 25°C a 0.10 M solution of NaOH has

$$pH = -\log_{10}\left(\frac{1.0 \times 10^{-14}}{0.10}\right) = -\log_{10}(1.0 \times 10^{-13}) = -(-13.00) = 13.00$$

As these examples show, calculating the pH is especially easy when the concentration of H_3O^+ is exactly a power of 10, because the logarithm is then just the power to which 10 is raised. In other cases we need a calculator. When we know the pH, we calculate the concentration of H_3O^+ by raising 10 to the power (−pH).

Because the most commonly encountered H_3O^+ concentrations are less than 1 M, the negative sign is put in the definition of the pH function to give a positive

FIGURE 15.3 A simple pH meter with a digital readout.



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value in most cases. A *high* pH means a *low* concentration of H_3O^+ and vice versa. At 25°C,

$$\text{pH} < 7 \qquad \text{Acidic solution} \qquad [15.3a]$$

$$\text{pH} = 7 \qquad \text{Neutral solution} \qquad [15.3b]$$

$$\text{pH} > 7 \qquad \text{Basic solution} \qquad [15.3c]$$

At other temperatures the pH of water differs from 7.00 (see Table 15.1). A change of one pH unit implies that the concentrations of H_3O^+ and OH^- change by a factor of 10 (that is, one order of magnitude). The pH is most directly measured with a **pH meter** (Fig. 15.3). The mechanism by which pH meters operate is described in Chapter 17. Figure 15.4 shows the pH values for several common fluids.

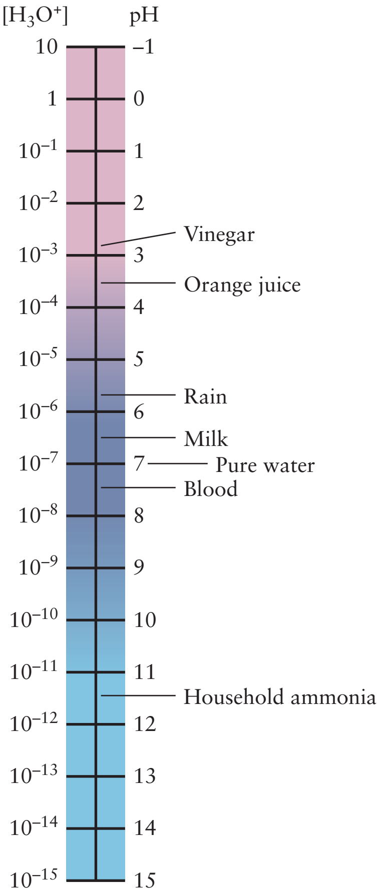


FIGURE 15.4 Many everyday materials are acidic or basic aqueous solutions with a wide range of pH values.

EXAMPLE 15.2

(a) A solution is prepared by dissolving 0.23 mol of NaH(*s*) in enough water to form 2.8 L of solution. Calculate its pH.

(b) The pH of some orange juice at 25°C is 2.85. Calculate $[H_3O^+]$ and $[OH^-]$.

SOLUTION

(a) Because H^- is a strong base, it reacts to give 0.23 mol of OH^-:

$$\text{NaH}(s) + \text{H}_2\text{O}(\ell) \longrightarrow \text{Na}^+(aq) + \text{OH}^-(aq) + \text{H}_2(g)$$

The concentration is

$$[\text{OH}^-] = \frac{0.23 \text{ mol}}{2.8 \text{ L}} = 8.2 \times 10^{-2} \text{ M}$$

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{8.2 \times 10^{-2}} = 1.22 \times 10^{-13} \text{ M}$$

The pH is then

$$\text{pH} = -\log_{10}(1.22 \times 10^{-13}) = 12.91$$

(b)

$$\text{pH} = 2.85 = -\log_{10}[\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-2.85}$$

This can be evaluated by using a calculator to give

$$[\text{H}_3\text{O}^+] = 1.4 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-3}} = 7.1 \times 10^{-12}$$

Related Problems: 13, 14, 15, 16

15.3 Acid and Base Strength

Hydrogen cyanide, HCN, is a highly toxic gas that dissolves in water to form equally toxic solutions of hydrocyanic acid.

Acids are classified as strong or weak, depending on the extent to which they are ionized in solution. In a **weak acid** the transfer of hydrogen ions to water does not proceed to completion. A weak acid such as acetic acid is thus also a **weak electrolyte;** its aqueous solutions do not conduct electricity as well as a strong acid of the same concentration because fewer ions are present. A weak acid shows smaller values for colligative properties than a strong acid (recall the effect of dissolved acetic acid on the freezing point of water in Fig. 11.13).

The Brønsted–Lowry theory helps to establish a quantitative scale for acid strength. The ionization of an acid (symbolized by "HA") in aqueous solution can be written as

$$\mathrm{HA}(aq) + \mathrm{H_2O}(\ell) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

where A^- is the conjugate base of HA. The equilibrium expression for this chemical reaction (see Section 14.2) is

$$\frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = K_a \qquad [15.4]$$

where the subscript "a" stands for "acid."[1] For example, if the symbol A^- refers to the cyanide ion (CN^-), we write

$$\frac{[\mathrm{H_3O^+}][\mathrm{CN^-}]}{[\mathrm{HCN}]} = K_a$$

where K_a is the **acid ionization constant** for hydrogen cyanide in water and has a numerical value of 6.17×10^{-10} at 25°C. Table 15.2 gives values of K_a, and the useful quantity $pK_a = -\log_{10} K_a$, for a number of important acids. The acid ionization constant is a quantitative measure of the strength of the acid in a given solvent (here, water). A strong acid has K_a greater than 1, so [HA] in the denominator is small and the acid ionizes almost completely. In a weak acid, K_a is smaller than 1 and the ionized species have low concentrations; the reaction with water proceeds to a limited extent before reaching equilibrium.

The strength of a base is inversely related to the strength of its conjugate acid; the weaker the acid, the stronger its conjugate base, and vice versa. To see this, note that the equation representing the ionization of a base such as ammonia in water can be written as

$$\underset{\text{Acid}_1}{\mathrm{H_2O}(\ell)} + \underset{\text{Base}_2}{\mathrm{NH_3}(aq)} \rightleftharpoons \underset{\text{Acid}_2}{\mathrm{NH_4^+}(aq)} + \underset{\text{Base}_1}{\mathrm{OH^-}(aq)}$$

which gives an equilibrium expression of the form

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

where the subscript "b" on K_b stands for "base." Because $[OH^-]$ and $[H_3O^+]$ are related through the water autoionization equilibrium expression

$$[\mathrm{OH^-}][\mathrm{H_3O^+}] = K_w$$

the K_b expression can be written as

$$K_b = \frac{[\mathrm{NH_4^+}]K_w}{[\mathrm{NH_3}][\mathrm{H_3O^+}]} = \frac{K_w}{K_a}$$

---

[1] $H_2O(\ell)$ is in its reference state, so it contributes the factor 1 (see Sections 14.2 and 14.3).

TABLE 15.2 Ionization Constants of Acids at 25°C

Acid	HA	A^-	K_a	pK_a
Hydroiodic	HI	I^-	$\sim 10^{11}$	~ -11
Hydrobromic	HBr	Br^-	$\sim 10^{9}$	~ -9
Perchloric	$HClO_4$	ClO_4^-	$\sim 10^{7}$	~ -7
Hydrochloric	HCl	Cl^-	$\sim 10^{7}$	~ -7
Chloric	$HClO_3$	ClO_3^-	$\sim 10^{3}$	~ -3
Sulfuric (1)	H_2SO_4	HSO_4^-	$\sim 10^{2}$	~ -2
Nitric	HNO_3	NO_3^-	~ 20	~ -1.3
Hydronium ion	H_3O^+	H_2O	1	0.0
Iodic	HIO_3	IO_3^-	1.6×10^{-1}	0.80
Oxalic (1)	$H_2C_2O_4$	$HC_2O_4^-$	5.9×10^{-2}	1.23
Sulfurous (1)	H_2SO_3	HSO_3^-	1.54×10^{-2}	1.81
Sulfuric (2)	HSO_4^-	SO_4^{2-}	1.2×10^{-2}	1.92
Chlorous	$HClO_2$	ClO_2^-	1.1×10^{-2}	1.96
Phosphoric (1)	H_3PO_4	$H_2PO_4^-$	7.52×10^{-3}	2.12
Arsenic (1)	H_3AsO_4	$H_2AsO_4^-$	5.0×10^{-3}	2.30
Chloroacetic	$CH_2ClCOOH$	CH_2ClCOO^-	1.4×10^{-3}	2.85
Hydrofluoric	HF	F^-	6.6×10^{-4}	3.18
Nitrous	HNO_2	NO_2^-	4.6×10^{-4}	3.34
Formic	$HCOOH$	$HCOO^-$	1.77×10^{-4}	3.75
Benzoic	C_6H_5COOH	$C_6H_5COO^-$	6.46×10^{-5}	4.19
Oxalic (2)	$HC_2O_4^-$	$C_2O_4^{2}-$	6.4×10^{-5}	4.19
Hydrazoic	HN_3	N_3^-	1.9×10^{-5}	4.72
Acetic	CH_3COOH	CH_3COO^-	1.76×10^{-5}	4.75
Propionic	CH_3CH_2COOH	$CH_3CH_2COO^-$	1.34×10^{-5}	4.87
Pyridinium ion	$HC_5H_5N^+$	C_5H_5N	5.6×10^{-6}	5.25
Carbonic (1)	H_2CO_3	HCO_3^-	4.3×10^{-7}	6.37
Sulfurous (2)	HSO_3^-	SO_3^{2-}	1.02×10^{-7}	6.91
Arsenic (2)	$H_2AsO_4^-$	$HAsO_4^{2-}$	9.3×10^{-8}	7.03
Hydrosulfuric	H_2S	HS^-	9.1×10^{-8}	7.04
Phosphoric (2)	$H_2PO_4^-$	HPO_4^{2-}	6.23×10^{-8}	7.21
Hypochlorous	$HClO$	ClO^-	3.0×10^{-8}	7.53
Hydrocyanic	HCN	CN^-	6.17×10^{-10}	9.21
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25
Carbonic (2)	HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.32
Arsenic (3)	$HAsO_4^{2-}$	AsO_4^{3}	3.0×10^{-12}	11.53
Hydrogen peroxide	H_2O_2	HO_2^-	2.4×10^{-12}	11.62
Phosphoric (3)	HPO_4^{2-}	PO_4^{3-}	2.2×10^{-13}	12.67
Water	H_2O	OH^-	1.0×10^{-14}	14.00

(1) and (2) indicate the first and second ionization constants, respectively.

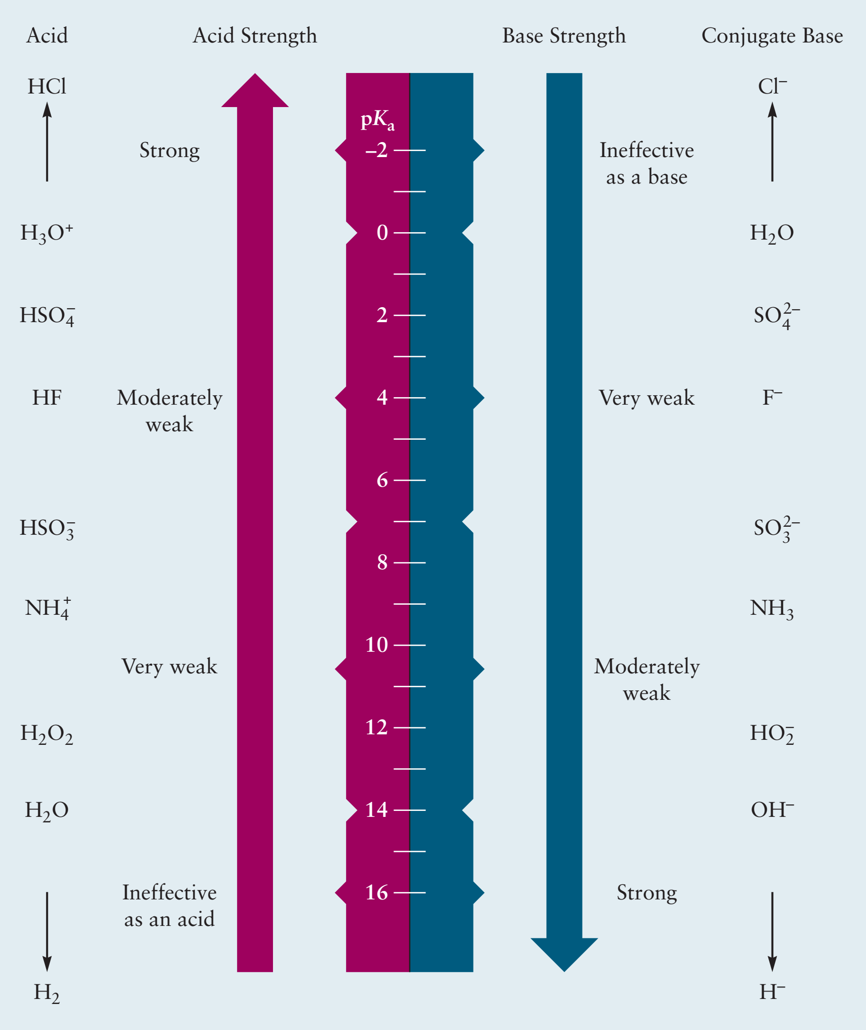
where K_a is the acid ionization constant for NH_4^+, the conjugate acid of the base NH_3. This general relationship between the K_b of a base and the K_a of its conjugate acid shows that K_b need not be tabulated separately from K_a, because the two are related through

$$K_w = K_a K_b \qquad [15.5]$$

It is also clear that if K_a is large (so that the acid is strong), then K_b is small (the conjugate base is weak). Figure 15.5 summarizes the strengths of conjugate acid–base pairs.

If two bases compete for hydrogen ions, the stronger base is favored in the equilibrium that is reached. The stronger acid donates hydrogen ions to the

FIGURE 15.5 The relative strengths of some acids and their conjugate bases.



stronger base, producing a weaker acid and a weaker base. To see this, consider the equilibrium

$$\underset{\text{Acid}_1}{HF(aq)} + \underset{\text{Base}_2}{CN^-(aq)} \rightleftharpoons \underset{\text{Acid}_2}{HCN(aq)} + \underset{\text{Base}_1}{F^-(aq)}$$

with equilibrium constant

$$\frac{[HCN][F^-]}{[HF][CN^-]} = K$$

The two bases F^- and CN^- compete for hydrogen ions. We can construct this net reaction by starting with one acid ionization reaction

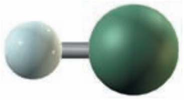
$$HF(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

$$\frac{[H_3O^+][F^-]}{[HF]} = K_a = 6.6 \times 10^{-4}$$

and *subtracting* from it a second acid ionization reaction:

$$HCN(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

$$\frac{[H_3O^+][CN^-]}{[HCN]} = K_a' = 6.17 \times 10^{-10}$$



Hydrogen fluoride, HF, is a colorless liquid that boils at 19.5°C. It dissolves in water to give solutions of hydrofluoric acid, a weak acid.

When the net reaction is the difference of two reactions, the equilibrium constant for the net reaction is the ratio of those for the separate reactions. (Section 14.4) The numerical value of K is

$$K = \frac{K_a}{K'_a} = \frac{6.6 \times 10^{-4}}{6.17 \times 10^{-10}} = 1.1 \times 10^6$$

Because HCN is a weaker acid than HF, K'_a is smaller than K_a, and K is larger than 1. The equilibrium described by K lies strongly to the right. The net result is donation of H^+ by the stronger acid (HF) to the stronger base (CN^-), to produce the weaker acid (HCN) and the weaker base (F^-). This example illustrates how the magnitudes of acid ionization constants can be used to predict the direction of net hydrogen ion transfer in reactions between acids and bases in aqueous solution.

Electronegativity and Oxoacid Strength

Trends in the relative strength of oxoacids are explained by the influence of electronegativity and bond polarity on the ease of donating a proton. The protons donated by **oxoacids** in aqueous solution were previously bonded to oxygen atoms on the acid molecule. Examples include sulfuric acid (H_2SO_4), nitric acid (HNO_3), and phosphoric acid (H_3PO_4). If the central atom is designated X, then oxoacids have the structure

$$—X—O—H$$

where X can be bonded to additional —OH groups, to oxygen atoms, or to hydrogen atoms. How does the strength of the oxoacid change as the electronegativity of X changes? Consider first the extreme case in which X is a highly electropositive element, such as an alkali metal. Of course, NaOH is not an acid at all, but a base. The sodium atom in Na—O—H gives up a full electron to make Na^+ and OH^- ions. Because the X—O bond here is almost completely ionic, the OH^- group has a net negative charge that holds the H^+ tightly to the oxygen and prevents formation of H^+ ions. The less electropositive alkaline-earth elements behave similarly. They form hydroxides, such as $Mg(OH)_2$, that are somewhat weaker bases than NaOH but in no way act as acids.

Now suppose the central atom X becomes more electronegative, reaching values between 2 and 3, as in the oxoacids of the elements B, C, P, As, S, Se, Br, and I. As X becomes more effective at withdrawing electron density from the oxygen atom, the X—O bond becomes more covalent. This leaves less negative charge on the oxygen atom, and consequently the oxoacid releases H^+ more readily (Fig. 15.6). Other things being equal, acid strength should increase with increasing electronegativity of the central atom. This trend is observed among the oxoacids listed in Table 15.2.

The strength of oxoacids with a given central element X increases with the number of lone oxygen atoms attached to the central atom. If the formula of these acids is written as $XO_n(OH)_m$, the corresponding acid strengths fall into distinct classes according to the value of n, the number of lone oxygen atoms (see

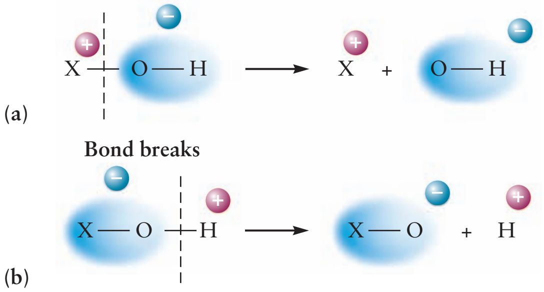


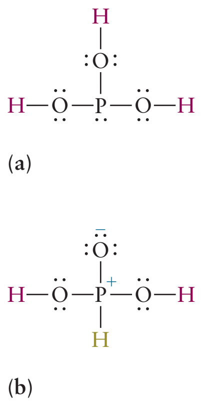
FIGURE 15.6 In part (a) the atom X is electropositive, so extra electron density (blue areas) accumulates on the OH group. The X—O bond then breaks easily, making the compound a base. In part (b) X is electronegative, so electron density is drawn from the H atom to the X—O bond. Now it is the O—H bond that breaks easily, and the compound is an acid.

TABLE 15.3 Acid Ionization Constants for Oxoacids of the Nonmetals

$X(OH)_m$ Very Weak	K_a	$XO(OH)_m$ Weak	K_a	$XO_2(OH)_m$ Strong	K_a	$XO_3(OH)_m$ Very Strong	K_a
$Cl(OH)$	3×10^{-8}	$H_2PO(OH)$	8×10^{-2}	$SeO_2(OH)_2$	10^3	$ClO_3(OH)$	2×10^7
$Te(OH)_6$	2×10^{-8}	$IO(OH)_5$	2×10^{-2}	$ClO_2(OH)$	5×10^2		
$Br(OH)$	2×10^{-9}	$SO(OH)_2$	2×10^{-2}	$SO_2(OH)_2$	1×10^2		
$As(OH)_3$	6×10^{-10}	$ClO(OH)$	1×10^{-2}	$NO_2(OH)$	2×10^1		
$B(OH)_3$	6×10^{-10}	$HPO(OH)_2$	1×10^{-2}	$IO_2(OH)$	1.6×10^1		
$Ge(OH)_4$	4×10^{-10}	$PO(OH)_3$	8×10^{-3}				
$Si(OH)_4$	2×10^{-10}	$AsO(OH)_3$	5×10^{-3}				
$I(OH)$	4×10^{-11}	$SeO(OH)_2$	3×10^{-3}				
		$TeO(OH)_2$	3×10^{-3}				
		$NO(OH)$	5×10^{-4}				

Table 15.3). Each increase of 1 in n increases the acid ionization constant K_a by a factor of about 10^5. Another way to describe this effect is to focus on the stability of the conjugate base, $XO_{n+1}(OH)^{-}_{m-1}$, of the oxoacid. The greater the number of lone oxygen atoms attached to the central atom, the more easily the net negative charge can be spread out over the ion, and therefore the more stable the base. This leads to a larger K_a.

An unusual and interesting structural result can be obtained from Table 15.3. Figure 15.7a shows the simplest Lewis diagram for phosphorous acid (H_3PO_3) in which each atom achieves an octet configuration. Such a diagram could also be written $P(OH)_3$ and would be analogous to $As(OH)_3$, which has no lone oxygen atoms bonded to the central atom ($n = 0$). On the basis of this analogy, we would expect the value of K_a for $P(OH)_3$ to be on the order of 10^{-9} (a very weak acid). But in fact, H_3PO_3 is only a moderately weak acid ($K_a = 1 \times 10^{-2}$) and fits better into the class of acids with one lone oxygen atom bonded to the central atom. X-ray diffraction measurements support this structural conclusion inferred from chemical behavior. So, the structure of H_3PO_3 is best represented by Figure 15.7b and corresponds either to a Lewis diagram with more than eight electrons around the central phosphorus atom or to one with formal charges on the central phosphorus and lone oxygen atoms. The formula of this acid is written as $HPO(OH)_2$ in Table 15.3. Unlike phosphoric acid (H_3PO_4), which is a triprotic acid, H_3PO_3 is a diprotic acid. The third hydrogen atom, the one directly bonded to the phosphorus atom, does not ionize even in strongly basic aqueous solution.


(a)

(b)

FIGURE 15.7 (a) The simplest Lewis diagram that can be drawn for H_3PO_3 gives an incorrect structure. This acid would be triprotic, like H_3PO_4. (b) The observed structure of H_3PO_3 requires assigning formal charge to the P atom and the lone O atom. The hydrogen atom attached to the P is not released into acid solution, so the acid is diprotic.

Indicators

An **indicator** is a soluble dye that changes color noticeably over a fairly narrow range of pH. The typical indicator is a weak organic acid that has a different color from its conjugate base (Fig. 15.8). Litmus changes from red to blue as its acid form is converted to base. Good indicators have such intense colors that only a


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FIGURE 15.8 Color differences in four indicators: bromophenol red, thymolphthalein, phenolphthalein, and bromocresol green. In each case the acidic form is on the left and the basic form is on the right.

few drops of a dilute indicator solution must be added to the solution being studied. The very low concentration of indicator molecules has almost no effect on the pH of solution. The color changes of the indicator reflect the effects of the *other* acids and bases present in the solution.

If the acid form of a given indicator is represented as HIn and the conjugate base form as In^-, their acid–base equilibrium is

$$HIn(aq) + H_2O(\ell) \rightleftarrows H_3O^+(aq) + In^-(aq) \qquad \frac{[H_3O^+][In^-]}{[HIn]} = K_a$$

where K_a is the acid ionization constant for the indicator. This expression can be rearranged to give

$$\frac{[H_3O^+]}{K_a} = \frac{[HIn]}{[In^-]} \qquad [15.6]$$

If the concentration of hydronium ion $[H_3O^+]$ is large relative to K_a, this ratio is large, and [HIn] is large compared with $[In^-]$. The solution has the color of the acid form of the indicator because most of the indicator molecules are in the acid form. Litmus, for example, has a K_a near 10^{-7}. If the pH is 5, then

$$\frac{[H_3O^+]}{K_a} = \frac{10^{-5}}{10^{-7}} = 100$$

Thus, approximately 100 times as many indicator molecules are in the acid form as in the base form, and the solution is red.

FIGURE 15.9 Indicators change their colors at very different pH values, so the best choice of indicator depends on the particular experimental conditions.

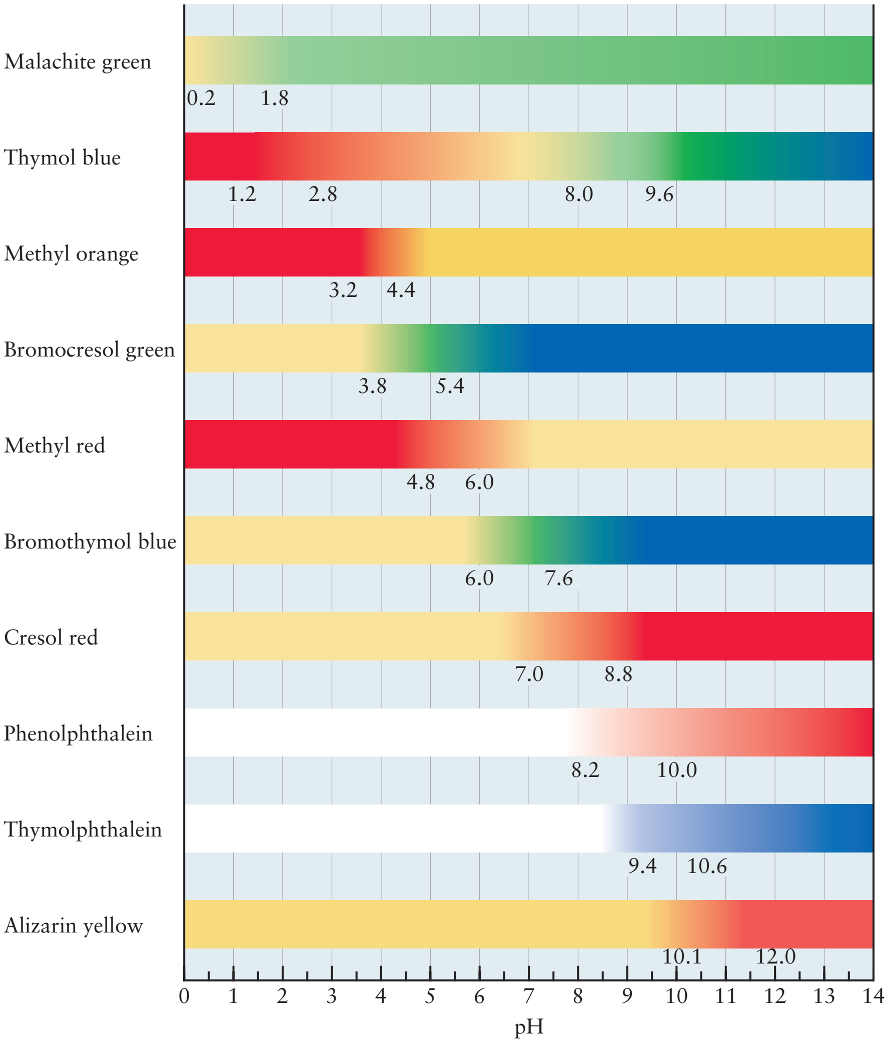

FIGURE 15.10 Red cabbage extract is a natural pH indicator. When the solution is highly acidic, the extract gives the solution a red color. As the solution becomes less and less acidic (more basic), the color changes from red to violet to yellow.

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As the concentration of hydronium ion is reduced, more molecules of acid indicator ionize to give the base form. When $[H_3O^+]$ is near K_a, almost equal amounts of the two forms are present and the color is a mixture of the colors of the two indicator states (violet for litmus). A further decrease in $[H_3O^+]$ to a value much smaller than K_a then leads to a predominance of the base form, with the corresponding color being observed.

Different indicators have different values for K_a and thus show color changes at different pH values (Fig. 15.9). The weaker an indicator is as an acid, the higher the pH at which the color change takes place. Such color changes occur over a range of 1 to 2 pH units. Methyl red, for example, is red when the pH is below 4.8 and yellow above 6.0; shades of orange are seen at intermediate pH values. This limits the accuracy to which the pH can be determined through the use of indicators. Section 15.6 shows that this fact does not affect the analytical determination of acid or base concentrations through titration, provided that an appropriate indicator is used.

Many natural dyes found in fruits, vegetables, and flowers act as pH indicators by changing color with changes in acidity (Fig. 15.10). A particularly striking example is cyanidin, which is responsible both for the red color of poppies and the blue color of cornflowers. The sap of the poppy is sufficiently acidic to turn cyanidin red, but the sap of the cornflower is basic and makes the dye blue. (See the image on page 625.) Related natural dyes called anthocyanins contribute to the colors of raspberries, strawberries, and blackberries.

15.4 Equilibria Involving Weak Acids and Bases

The reactions of weak acids and bases with water do not go to completion. So, to calculate the pH of their solutions, we use K_a or K_b and the laws of chemical equilibrium. The calculations follow the pattern of Example 14.10 for gas equilibria. In that case the initial gas-phase pressures $P°$ are known, and we calculate the pressures of products resulting from the incomplete reaction. Here we know the initial concentration of acid or base, and calculate the concentrations of products resulting from its partial reaction with water.

Weak Acids

A weak acid has a K_a smaller than 1. Values of the pK_a start at zero for the strongest weak acid and range upward. (If the pK_a is greater than 14, the compound is ineffective as an acid in aqueous solution.) When a weak acid is dissolved in water, the original concentration is almost always known but partial reaction with water consumes some HA and generates A^- and H_3O^+:

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

To calculate the amounts of H_3O^+, A^-, and HA at equilibrium, we use the methods of Chapter 14, with partial pressures replaced by concentrations. A new feature here is that one of the products (H_3O^+) can also come from a second source, the autoionization of the solvent, water. In most of the applications we study, this second effect is small and can be neglected in the equations. Even so, it is a good idea to verify at the end of each calculation that the $[H_3O^+]$ from the acid ionization alone exceeds 10^{-7} M by at least one order of magnitude. Otherwise, we have to use the more complete method of analysis given in Section 15.8.

EXAMPLE 15.3

Acetic acid (CH_3COOH) has a K_a of 1.76×10^{-5} at 25°C. Suppose 1.000 mol is dissolved in enough water to give 1.000 L of solution. Calculate the pH and the fraction of acetic acid ionized at equilibrium.

SOLUTION

The initial concentration of acetic acid is 1.000 M. If y mol L^{-1} ionizes, then

	$CH_3COOH(aq)$ + $H_2O(\ell)$ $\rightleftharpoons$	$H_3O^+(aq)$ +	$CH_3COO^-(aq)$
Initial concentration (M)	1.000	≈0	0
Change in concentration (M)	$-y$	$+y$	$+y$
Equilibrium concentration (M)	$1.000 - y$	y	y

Note that we ignored the H_3O^+ initially present from the ionization of water because we expect it to be smaller than y for all but the weakest acids or the most dilute solutions. Then, the equilibrium expression states that

$$\frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{y^2}{1.000 - y} = K_a = 1.76 \times 10^{-5}$$

This equation could be solved using the quadratic formula, as we did in Chapter 14. A quicker way is based on the fact that acetic acid is a weak acid and therefore only a small fraction is ionized at equilibrium. Therefore it is reasonable to assume that y is small relative to 1.000 (that is, the final equilibrium concentration of CH_3COOH is close to its initial concentration). This gives

$$\frac{y^2}{1.000 - y} \approx \frac{y^2}{1.000} = 1.76 \times 10^{-5}$$

$$y = 4.20 \times 10^{-3}$$

so

$$[H_3O^+] = y = 4.20 \times 10^{-3} \text{ M}$$

Now we have to check whether the approximations are indeed valid. First, y is indeed much smaller than the original concentration of 1.000 M (by a factor of 200), so neglecting it in the denominator is justified. Second, the concentration of H_3O^+ from acetic acid (4.2×10^{-3} M) is large compared with 10^{-7} M, so neglecting the water ionization is also justified. Therefore,

$$\text{pH} = -\log_{10}(4.2 \times 10^{-3}) = 2.38$$

The fraction ionized is the ratio of the concentration of CH_3COO^- present at equilibrium to the concentration of CH_3COOH present in the first place:

$$\frac{y}{1.000} = y = 4.2 \times 10^{-3}$$

The percentage of the acetic acid that is ionized is 0.42%. Fewer than one in a hundred of the molecules of this typical weak acid dissociate in this solution.

Related Problems: 27, 28, 29, 30

Approximation methods of the type used in this example are also used in Example 14.6 and are discussed more extensively in Appendix C. As the solution of a weak acid becomes more dilute, a greater fraction of it ionizes, as shown by the following example.

EXAMPLE 15.4

Suppose that 0.00100 mol of acetic acid is used instead of the 1.000 mol in the preceding example. Calculate the pH and the percentage of acetic acid ionized.

SOLUTION

Once again we assume that the contribution of the ionization of water to $[H_3O^+]$ is negligible, and check the validity of the assumption at the end of the calculation. Hence,

$$[CH_3COOH] = 0.00100 - y$$

$$[CH_3COO^-] = [H_3O^+] = y$$

$$\frac{y^2}{0.00100 - y} = 1.76 \times 10^{-5}$$

In this case, y is *not* small relative to 0.00100 because a substantial fraction of the acetic acid molecules ionizes, so y cannot be neglected in the denominator. There are two alternatives for solving the problem in this case.

The first method is to solve the quadratic equation obtained by multiplying out the equilibrium expression:

$$y^2 + (1.76 \times 10^{-5})y - (1.76 \times 10^{-8}) = 0$$

Using of the quadratic formula gives

$$y = 1.24 \times 10^{-4} \text{ M} = [H_3O^+] = [CH_3COO^-]$$

Because $y \gg 10^{-7}$ M, neglecting water ionization in setting up the problem is justified.

$$\text{pH} = -\log_{10}(1.24 \times 10^{-4}) = 3.91$$

$$\text{percentage ionized} = \frac{1.24 \times 10^{-4}\text{ M}}{0.00100\text{ M}} \times 100\% = 12.4\%$$

The other approach to solving the problem is to use successive approximations (see Appendix C). Begin by neglecting y in the denominator (relative to 0.00100), which gives

$$\frac{y^2}{0.00100} = 1.76 \times 10^{-5}$$

$$y = 1.33 \times 10^{-4}\text{ M}$$

This is just what we do in Example 15.3. Now, continue by reinserting this *approximate* value of y into the *denominator* and then recalculate y:

$$\frac{y^2}{0.00100 - 0.00133} = 1.76 \times 10^{-5}$$

$$y^2 = 1.53 \times 10^{-8}$$

$$y = 1.33 \times 10^{-4}\ \text{M}$$

If we insert this new value of y into the denominator and iterate the calculation once again, we obtain 1.24×10^{-4} M, the same value produced by the quadratic formula. We terminate the iteration process when two successive results for y agree to the desired number of significant figures.

Related Problems: 31, 32

The method of successive approximations is often faster to apply than the quadratic formula. Keep in mind that the accuracy of a result is limited both by the accuracy of the input data (values of K_a and initial concentrations) and by the fact that solutions are not ideal. It is pointless to calculate equilibrium concentrations to any degree of accuracy higher than 1% to 3%.

Weak Bases

There is a perfect parallel between the behavior of weak bases and weak acids. The definition and description of weak acids, the existence of K_a, and the production of $H_3O^+(aq)$ ion when they are dissolved in water can be applied directly to weak bases, the existence of K_b, and the production of $OH^-(aq)$ ion. A **weak base** such as ammonia reacts only partially with water to produce $OH^-(aq)$:

$$H_2O(\ell) + NH_3(aq) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

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

The K_b of a weak base is smaller than 1, and the weaker the base, the smaller the K_b. If the K_b of a compound is smaller than 1×10^{-14}, that compound is ineffective as a base in aqueous solution.

The analogy to weak acids continues in the calculation of the aqueous equilibria of weak bases, as the following example shows.

EXAMPLE 15.5

Calculate the pH of a solution made by dissolving 0.0100 mol of NH_3 in enough water to give 1.000 L of solution at 25°C. The K_b for ammonia is 1.8×10^{-5}.

SOLUTION

Set up the table of the changes in concentrations that occur as the reaction goes to equilibrium, neglecting the small contribution to $[OH^-]$ from the autoionization of water:

	$H_2O(\ell) + NH_3(aq)$	$\rightleftarrows NH_4^+(aq)$	$+ OH^-(aq)$
Initial concentration (M)	0.0100	0	≈0
Change in concentration (M)	$-y$	$+y$	$+y$
Equilibrium concentration (M)	$0.100 - y$	y	y

Substitution into the equilibrium expression gives

$$\frac{y^2}{0.0100 - y} = K_b = 1.8 \times 10^{-5}$$

which can be solved for y by either the quadratic formula or the method of successive approximations to obtain:

$$y = 4.15 \times 10^{-4} \text{ M} = [\text{OH}^-]$$

The product of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ is always K_w. Hence,

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{4.15 \times 10^{-14}} = 2.4 \times 10^{-11}$$

$$\text{pH} = -\log_{10}(2.4 \times 10^{-11}) = 10.62$$

The pH is greater than 7, as expected for a solution of a base.

Related Problems: 35, 36

Hydrolysis

Most of the acids considered up to now have been uncharged species with the general formula HA. In the Brønsted–Lowry picture there is no reason why the acid should be an electrically neutral molecule. When NH_4Cl, a salt, dissolves in water, NH_4^+ ions are present. These ionize partially by transferring hydrogen ions to water, a straightforward Brønsted–Lowry acid–base reaction:

$$\underset{\text{Acid}_1}{\text{NH}_4^+(aq)} + \underset{\text{Base}_2}{\text{H}_2\text{O}(\ell)} \rightleftharpoons \underset{\text{Acid}_2}{\text{H}_3\text{O}^+(aq)} + \underset{\text{Base}_1}{\text{NH}_3(aq)}$$

$$\frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{\text{NH}_4^+} = K_a = 5.6 \times 10^{-10}$$

NH_4^+ acts as an acid here, just as acetic acid did in Examples 15.3 and 15.4. Because K_a is much smaller than 1, only a small amount of H_3O^+ is generated. NH_4^+ is a weak acid, but it is nonetheless an acid, and a solution of ammonium chloride has a pH below 7 (Fig. 15.11).

(a) (b) (c)

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FIGURE 15.11 Proof that ammonium chloride is an acid. (a) A solution of sodium hydroxide, with the pink color of phenolphthalein indicating its basic character. (b and c) As aqueous ammonium chloride is added, a neutralization reaction takes place and the solution turns colorless from the bottom up.

Hydrolysis is the label for the reaction of a substance with water. This term is applied especially to a reaction in which the pH changes from 7 upon dissolving a salt (in this case, NH_4Cl) in water. There is no need for any special description of hydrolysis. The hydrolysis that takes place when NH_4Cl dissolves in water is completely described as a Brønsted–Lowry reaction in which water acts as a base and NH_4^+ acts as an acid to give a pH below 7. In parallel fashion, dissolving a salt whose anion is a weak base produces a basic solution. This too is a case of hydrolysis; it is simply another Brønsted–Lowry acid–base reaction, with water acting now as an acid (a hydrogen ion donor).

Two salts that give basic solutions are sodium acetate and sodium fluoride. When these salts dissolve in water, they furnish acetate (CH_3COO^-) and fluoride (F^-) ions, respectively, both of which act as Brønsted–Lowry bases,

$$H_2O(\ell) + CH_3COO^-(aq) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

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

causing the OH^- concentration to increase and give a pH above 7.

EXAMPLE 15.6

Suppose 0.100 mol of $NaCH_3COO$ is dissolved in enough water to make 1.00 L of solution. What is the pH of the solution?

SOLUTION

The K_a for CH_3COOH, the conjugate acid of CH_3COO^-, is 1.76×10^{-5}. Therefore, K_b for the acetate ion is

$$\frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = K_b = \frac{K_w}{K_a} = 5.7 \times 10^{-10}$$

The equilibrium here is

	$H_2O(\ell) + CH_3COO^-(aq)$	$\rightleftharpoons CH_3COOH(aq)$	$+\ OH^-(aq)$
Initial concentration (M)	0.100	0	≈0
Change in concentration (M)	$-y$	$+y$	$+y$
Equilibrium concentration (M)	$0.100 - y$	y	y

Substitution into the equilibrium expression gives

$$\frac{y^2}{0.100 - y} = K_b = 5.7 \times 10^{-10}$$

$$y = 7.5 \times 10^{-6}\ \text{M} = [OH^-]$$

Note that y is small relative to 0.100 and fairly large relative to 10^{-7}.

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{7.5 \times 10^{-6}} = 1.3 \times 10^{-9}\ \text{M}$$

$$\text{pH} = 8.89$$

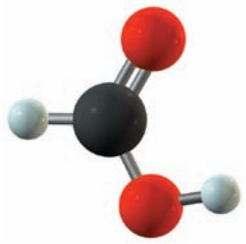
Related Problems: 41, 42

Hydrolysis does not occur with all ions, only with those that are conjugate acids of weak bases or conjugate bases of weak acids. Chloride ion is the conjugate base of the strong acid HCl and consequently is ineffective as a base, unlike $F^-(aq)$ and $CH_3COO^-(aq)$. Its interaction with water would therefore scarcely change the $OH^-(aq)$ concentration. So, a solution of NaCl is neutral, whereas a solution of NaF is slightly basic.

15.5 Buffer Solutions

A **buffer solution** is any solution that maintains approximately constant pH upon small additions of acid or base. Typically, a buffer solution contains a weak acid and its conjugate weak base in approximately equal concentrations. Buffer solutions play important roles in controlling the solubility of ions in solution (see Chapter 16) and in maintaining the pH in biochemical and physiological processes. Many life processes are sensitive to pH and require regulation within a small range of H_3O^+ and OH^- concentrations. Organisms have built-in buffers to protect them against large changes in pH. Human blood has a pH near 7.4, which is maintained by a combination of carbonate, phosphate, and protein buffer systems. A blood pH below 7.0 or above 7.8 leads quickly to death.

Calculations of Buffer Action



Formic acid, HCOOH, is the simplest carboxylic acid, with only a hydrogen atom attached to the —COOH.

Consider a typical weak acid, formic acid (HCOOH), and its conjugate base, formate ion ($HCOO^-$). The latter can be obtained by dissolving a salt such as sodium formate (NaHCOO) in water. The acid–base equilibrium established between these species is given by

$$HCOOH(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$$

with an acid ionization constant

$$\frac{[H_3O^+][HCOO^-]}{[HCOOH]} = K_a = 1.77 \times 10^{-4}$$

Section 15.2 describes the pH of a solution containing only a weak acid (such as HCOOH) or only a weak base (such as $HCOO^-$). Suppose now that the weak acid and its conjugate base are *both* present initially. The resulting calculations resemble closely the calculation of Example 14.15, in which equilibrium was established from an initial mixture containing both reactants and products.

EXAMPLE 15.7

Suppose 1.00 mol of HCOOH and 0.500 mol of NaHCOO are added to water and diluted to 1.00 L. Calculate the pH of the solution.

SOLUTION

	$HCOOH(aq)$ + $H_2O(\ell)$ $\rightleftharpoons$	$H_3O^+(aq)$ +	$HCOO^-(aq)$
Initial concentration (M)	1.00	≈0	0.500
Change in concentration (M)	$-y$	$+y$	$+y$
Equilibrium concentration (M)	$1.00 - y$	y	$0.500 + y$

The equilibrium expression is

$$\frac{y(0.500 + y)}{1.00 - y} = K_a = 1.77 \times 10^{-4}$$

Because y is likely to be small relative to 1.00 and to 0.500, we write the approximate expression

$$\frac{y(0.500)}{1.00} \approx 1.77 \times 10^{-4}$$

$$y \approx 3.54 \times 10^{-4} \text{ M} = [H_3O^+]$$

A glance verifies that y is indeed small relative to 1.00 and 0.500. Then

$$\text{pH} = -\log_{10}(3.54 \times 10^{-4}) = 3.45$$

Related Problems: 43, 44

To understand how buffer solutions work, let's write the equilibrium expression for the ionization of a weak acid HA in the form

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

The concentration of hydronium ion depends on the ratio of the concentration of the weak acid to the concentration of its conjugate base. The key to effective buffer action is to keep these concentrations nearly equal and fairly large. Adding a small amount of base to an effective buffer takes away only a few percent of the HA molecules by converting them into A^- ions and adds only a few percent to the amount of A^- originally present. The ratio $[HA]/[A^-]$ decreases, but only very slightly. Added acid consumes a small fraction of the base A^- to generate a bit more HA. The ratio $[HA]/[A^-]$ now increases, but again the change is only slight. Because the concentration of H_3O^+ is tied directly to this ratio, it changes only slightly. The following example illustrates buffer action quantitatively.

EXAMPLE 15.8

Suppose 0.10 mol of a strong acid such as HCl is added to the solution in Example 15.7. Calculate the pH of the resulting solution.

SOLUTION

The strong acid HCl ionizes essentially completely in dilute aqueous solution. Initially assume that *all* the hydrogen ions from HCl are taken up by formate ions to produce formic acid, some of which ionizes back to formate ion and H_3O^+. This is simply a way of describing one possible route by which equilibrium is approached and does not define the sequence of reactions that actually occurs. The position of the final equilibrium does not depend on the route by which it is attained.

Because 0.10 mol of HCl reacts with an equal number of moles of $HCOO^-$, the concentrations of $HCOO^-$ and HCOOH *before* ionization are

$$[HCOO^-]_0 = 0.50 - 0.10 = 0.40 \text{ M}$$

$$[HCOOH]_0 = 1.00 + 0.10 = 1.10 \text{ M}$$

The table to calculate the concentrations at equilibrium is

	$HCOOH(aq)$ +	$H_2O(\ell) \rightleftharpoons$	$H_3O^+(aq)$ +	$HCOO^-(aq)$
Initial concentration (M)	1.10		≈0	0.40
Change in concentration (M)	$-y$		$+y$	$+y$
Equilibrium concentration (M)	$1.10 - y$		y	$0.40 + y$

The equilibrium expression then becomes

$$\frac{y(0.40 + y)}{1.10 - y} = 1.77 \times 10^{-4}$$

Because y is again likely to be small relative to both 0.40 and 1.10,

$$y \approx \left(\frac{1.10}{0.40}\right)(1.77 \times 10^{-4}) = 4.9 \times 10^{-4}$$

$$\text{pH} = 3.31$$

Even though 0.10 mol of a strong acid was added, the pH changed only slightly, from 3.45 to 3.31. In contrast, the same amount of acid added to a liter of pure water would change the pH from 7 to 1.

Related Problems: 45, 46

Note that we solved this problem by first performing a stoichiometric (limiting reactant) calculation and then an equilibrium calculation. A similar strategy works if a strong base such as OH^- is added instead of a strong acid. The base reacts with formic acid to produce formate ions. Adding 0.10 mol of OH^- to the $HCOOH/HCOO^-$ buffer of Example 15.7 increases the pH only to 3.58. In the absence of the buffer system, the same base would raise the pH to 13.00.

In any buffer there is competition between the tendency of the acid to donate hydrogen ions to water (increasing the acidity) and the tendency of the base to accept hydrogen ions from water (increasing the basicity). The resulting pH depends on the magnitude of K_a. If K_a is large relative to 10^{-7}, the acid ionization will win out and acidity will increase, as in the $HCOOH/HCOO^-$ buffer. A basic buffer (with pH > 7) can be prepared by working with an acid–base pair with K_a smaller than 10^{-7}. In this case the net reaction produces OH^-, and we must use K_b to determine the equilibrium state. A typical example is the NH_4^+/NH_3 buffer prepared by mixing ammonium chloride with ammonia.

EXAMPLE 15.9

Calculate the pH of a solution made by adding 0.100 mol of NH_4Cl and 0.200 mol of NH_3 to water and diluting to 1.000 L. K_a for NH_4^+ is 5.6×10^{-10}.

SOLUTION

Because $K_a \ll 10^{-7}$ for NH_4^+ (equivalently, $K_b \gg 10^{-7}$ for NH_3), the net reaction is production of OH^- ions. Therefore, the equilibrium is written to show the net transfer of hydrogen ions from water to NH_3:

	$H_2O(\ell) + NH_3(aq)$	$\rightleftarrows NH_4^+(aq)$	$+ OH^-(aq)$
Initial concentration (M)	0.200	0.100	0
Change in concentration (M)	$-y$	$+y$	$+y$
Equilibrium concentration (M)	$0.200 - y$	$0.100 + y$	y

The equilibrium expression is

$$\frac{y(0.100 + y)}{0.200 - y} = K_b = \frac{K_w}{K_a} = 1.8 \times 10^{-5}$$

If y is small relative to the original concentrations of both NH_3 and NH_4^+, then

$$\frac{y(0.100)}{0.200} \approx 1.8 \times 10^{-5}$$

$$y \approx \left(\frac{0.200}{0.100}\right)(1.8 \times 10^{-5}) = 3.6 \times 10^{-5} \ll 0.100, 0.200$$

$$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]} = \frac{1.0 \times 10^{-14}}{3.6 \times 10^{-5}} = 2.8 \times 10^{-10} \text{ M}$$

$$\text{pH} = -\log_{10}(2.8 \times 10^{-10}) = 9.55$$

Designing Buffers

Control of pH is vital in synthetic and analytical chemistry, just as it is in living organisms. Procedures that work well at a pH of 5 may fail when the concentration of hydronium ion in the solution is raised tenfold to make the pH 4. Fortunately, it is possible to prepare buffer solutions that maintain the pH close to any desired value by the proper choice of a weak acid and the ratio of its concentration to that of its conjugate base. Let's see how to choose the best conjugate acid–base system and how to calculate the required acid–base ratio.

In Examples 15.7, 15.8, and 15.9, the equilibrium concentrations of acid and base in the buffer systems were close to the initial concentrations. When this is the case, the calculation of pH is simplified greatly, because for either an acidic *or* a basic buffer,

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \approx \frac{[H_3O^+][A^-]_0}{[HA]_0}$$

$$[H_3O^+] \approx \frac{[HA]_0}{[A^-]_0}K_a$$

and the pH is given by

$$\text{pH} \approx \text{p}K_a - \log_{10}\frac{[HA]_0}{[A^-]_0} \qquad \textbf{[15.7]}$$

We obtained Equation 15.7 by taking the logarithm and changing sign. It is easy to verify that this simple equation gives the correct result for the three preceding examples. However, it must be used with some care because it is only approximate. It is valid only when *both* $[H_3O^+]$ and $[OH^-]$ are small relative to $[HA]_0$ and $[A^-]_0$; this means the extent of ionization must be small.

We can use this expression relating pH to pK_a to design buffers with a specific value of pH. In an optimal buffer the acid and its conjugate base are purposely very nearly equal in concentration; if the difference in concentrations is too great, the buffer is less resistant to the effects of adding acid or base. To select a buffer system, we choose an acid with a pK_a as close as possible to the desired pH. Then we adjust the concentrations of acid and conjugate base to give exactly the desired pH.

EXAMPLE 15.10

Design a buffer system with pH 4.60.

SOLUTION

From Table 15.2, the pK_a for acetic acid is 4.75, so the CH_3COOH/CH_3COO^- buffer is a suitable one. The concentrations required to give the desired pH are related by

$$\text{pH} = 4.60 = \text{p}K_a - \log_{10}\frac{[CH_3COOH]_0}{[CH_3COO^-]_0}$$

$$\log_{10}\frac{[CH_3COOH]_0}{[CH_3CHOO^-]_0} = \text{p}K_a - \text{pH} = 4.75 - 4.60 = 0.15$$

$$\frac{[CH_3COOH]_0}{[CH_3COO^-]_0} = 10^{0.15} = 1.4$$

We can establish this ratio by dissolving 0.100 mol of sodium acetate and 0.140 mol of acetic acid in water and diluting to 1.00 L, or 0.200 mol of $NaCH_3COO$ and 0.280 mol of CH_3COOH in the same volume, and so on. As long as the ratio of the concentrations is 1.4, the solution will be buffered at approximately pH 4.60.

Related Problems: 47, 48, 49, 50

The preceding example shows that the *absolute* concentrations of acid and conjugate base in a buffer are much less important than is their ratio in determining the pH. Nonetheless, the absolute concentrations do affect the capacity of the solution to resist changes in pH when acid or base is added. The higher the concentrations of buffering species, the smaller the change in pH when a fixed amount of a

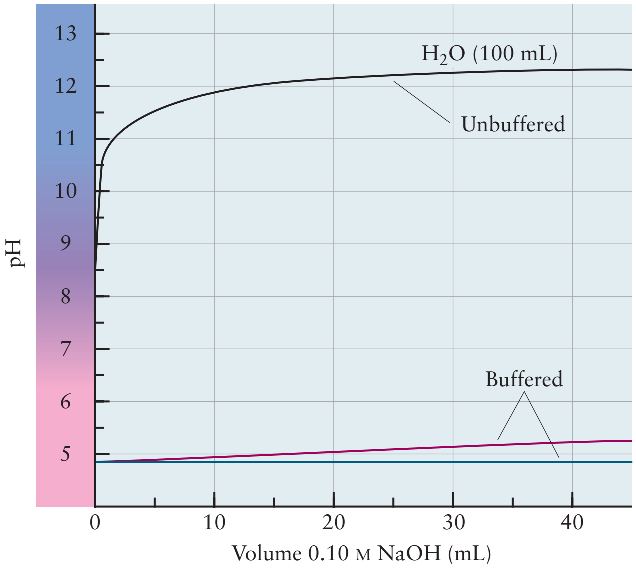


FIGURE 15.12 Addition of a given volume of base to buffered and unbuffered solutions causes a much greater change in the pH of the unbuffered solution. Of the two buffered solutions, the one with higher buffer concentration resists pH changes more effectively. The red line represents 100 mL of a buffer that is 0.1 M in both CH_3COOH and CH_3COO^-; the blue line represents the same volume of a buffer that is 1.0 M in both components.

strong acid or base is added. In Example 15.7 a change in buffer concentrations from 1.00 M and 0.500 M to 0.500 M and 0.250 M does not alter the original pH of 3.45 because the ratio of acid to base concentrations is unchanged. The pH after 0.100 mol of HCl is added does change to the value 3.15 rather than 3.31. The buffer at lower concentration is less resistant to pH change (Fig. 15.12). The buffering capacity of *any* buffer solution is exhausted if enough strong acid (or strong base) is added to use up the original amount of weak base (or weak acid) through chemical reaction.

15.6 Acid–Base Titration Curves

Section 11.3 describes an acid–base titration as the addition of carefully metered volumes of a basic solution of known concentration to an acidic solution of unknown concentration—or the addition of acid to base—to reach an *endpoint* at which the unknown solution has been completely neutralized. The endpoint is signaled by the color change of an indicator or by a sudden rise or fall in pH. The pH of the reaction mixture changes continuously over the course of an acid–base titration, but changes abruptly only near the end point. A graph of the pH versus the volume V of titrating solution added is a **titration curve.** Its shape depends on the value of K_a and on the concentrations of the acid and base reacting. The concepts and tools of acid–base equilibria predict the exact shapes of titration curves when these quantities are all known. The same concepts allow K_a and the concentration of the unknown solution to be calculated from an experimental titration curve. Here we examine three categories of titration and determine the titration curve for each: strong acid reacting with strong base, weak acid reacting with strong base, and strong acid reacting with weak base. Titrations of a weak acid with a weak base (and the reverse) are not useful for analytical purposes.

Titration of a Strong Acid with a Strong Base

The addition of a strong base to a strong acid (or the reverse) is the simplest type of titration. The chemical reaction is the neutralization:

$$H_3O^+(aq) + OH^-(aq) \longrightarrow 2\ H_2O(\ell)$$

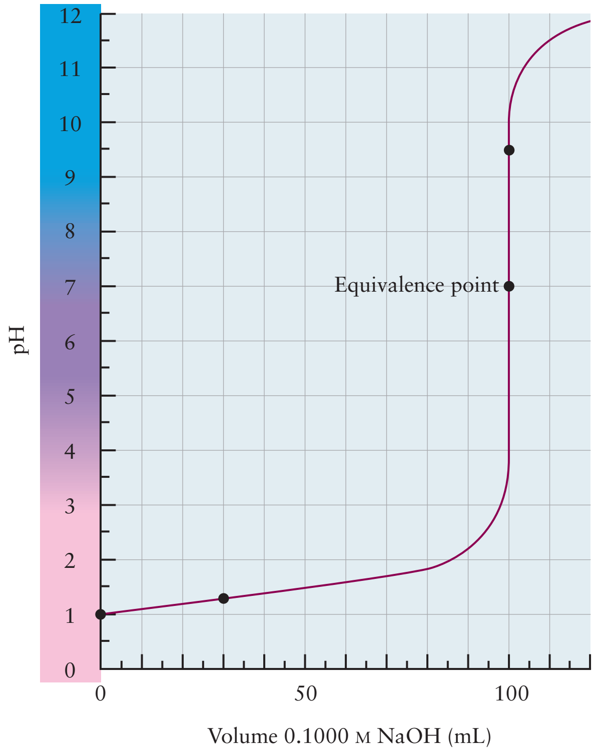


FIGURE 15.13 A titration curve for the titration of a strong acid by a strong base. The curve shown is for 100.0 mL of 0.1000 M HCl titrated with 0.1000 M NaOH.

Suppose a solution of 100.0 mL (0.1000 L) of 0.1000 M HCl is titrated with 0.1000 M NaOH. What does the titration curve look like? The curve can be measured experimentally, and the result is shown in Figure 15.13. We can also construct the curve theoretically by calculating the pH of the reaction mixture at many different points during the addition of the NaOH solution and plotting the results. The following example illustrates the theoretical procedure.

1. ***V* = 0 mL NaOH added**
   Initially, $[H_3O^+] = 0.1000$ M, so the pH is 1.000. The number of moles of H_3O^+ present initially is

$$n_{H_3O^+} = [H_3O^+](\text{volume}) = (0.1000 \text{ mol L}^{-1})(0.1000 \text{ L})$$
$$= 1.000 \times 10^{-2} \text{ mol}$$

2. ***V* = 30.00 mL NaOH added**
   30.00 mL of 0.1000 M NaOH solution contains

$$(0.1000 \text{ mol L}^{-1})(0.03000 \text{ L}) = 3.000 \times 10^{-3} \text{ mol OH}^-$$

This reacts with (and neutralizes) an equal number of moles of the H_3O^+ ion present initially and reduces $n_{H_3O^+}$ to

$$n_{H_3O^+} = (1.000 \times 10^{-2} - 3.000 \times 10^{-3})\text{mol} = 7.00 \times 10^{-3} \text{ mol}$$

In addition—and this is very important to remember—the volume of the titration mixture has increased from 100.0 to 130.0 mL (that is, from 0.1000 to 0.1300 L). The concentration of H_3O^+ at this point in the titration is

$$[H_3O^+] = \frac{n_{H_3O^+}}{V_{\text{tot}}} = \frac{7.00 \times 10^{-3} \text{ mol}}{0.1300 \text{ L}} = 0.0538 \text{ M}$$
$$\text{pH} = 1.27$$

3. ***V* = 100.00 mL NaOH added**
   This is called the **equivalence point,** that point in the titration at which the number of moles of base added equals the number of moles of acid originally present. The volume of base added up to the equivalence point is the **equivalent**

volume, V_e. At the equivalence point in the titration of a strong acid with a strong base, the concentrations of OH^- and H_3O^+ must be equal and the pH 7.0 due to the autoionization of water. At this point the solution is simply a nonhydrolyzing salt (in this case, NaCl) in water. The pH is 7 at the equivalence point only in the titration of a strong acid with a strong base (or vice versa). The pH at the equivalence point differs from 7 if the titration involves a weak acid or weak base.

4. **V = 100.05 mL NaOH added**

   Beyond the equivalence point, OH^- is added to a neutral unbuffered solution. The OH^- concentration can be found from the number of moles of OH^- added after the equivalence point has been reached. The volume beyond the equivalence point at this stage is 0.05 mL, or 5×10^{-5} L. (This is the volume of approximately one drop of solution added from the buret.) The number of moles of OH^- in this volume is

   $$(0.1000 \text{ mol L}^{-1})(5 \times 10^{-5} \text{ L}) = 5 \times 10^{-6} \text{ mol}$$

   Meanwhile, the total volume of the titration mixture is

   $$0.1000 \text{ L HCl solution} + 0.10005 \text{ L NaOH solution} = 0.20005 \text{ L solution}$$

   Therefore, the concentration of OH^- is

   $$[OH^-] = \frac{\text{moles OH}^-}{\text{total volume}} = \frac{5 \times 10^{-5} \text{ mol}}{0.2005 \text{ L}} = 2.5 \times 10^{-5} \text{ M}$$

   $$[H_3O^+] = 4 \times 10^{-10} \text{ M}; \quad \text{pH} = 9.4$$

As the titration curve shows (see Fig. 15.13), the pH increases dramatically in the immediate vicinity of the equivalence point: $[H_3O^+]$ changes by four orders of magnitude between 99.98 mL and 100.02 mL NaOH! Any indicator whose color changes between pH = 5.0 and pH = 9.0 therefore signals the endpoint of the titration to an accuracy of ±0.02 mL in 100.0 mL, or ±0.02%. The titration **endpoint,** the experimentally measured volume at which the indicator changes color, is then almost identical to the equivalence point, the theoretical volume at which the chemical amount of added base equals that of acid present originally.

The titration of a strong base by a strong acid is entirely parallel. In this case the pH starts at a higher value and *drops* through a pH of 7 at the equivalence point. The roles of acid and base, and of H_3O^+ and OH^-, are reversed in the equations already given.

Titration of a Weak Acid with a Strong Base

We turn now to the titration of a weak acid with a strong base (the titration of a weak base with a strong acid is analogous). The equivalence point has the same meaning as for a strong acid titration. At the equivalence point, the number of moles of base added (in volume V_e) is equal to the number of moles of acid originally present (in volume V_0). So, once again

$$c_0 V_0 = c_t V_e$$

where c_0 is the original weak acid concentration and c_t is the OH^- concentration in the titrating solution.

The calculation of the titration curve differs from the strong acid–strong base case in that now equilibrium (reflected in the K_a of the weak acid) enters the picture. As an example, consider the titration of 100.0 mL of a 0.1000 M solution of acetic acid (CH_3COOH) with 0.1000 M NaOH. For this titration,

$$V_e = \frac{c_0}{c_t} V_0 = \left(\frac{0.1000 \text{ M}}{0.1000 \text{ M}}\right)(100.0 \text{ mL})$$

$$= 100.0 \text{ mL}$$

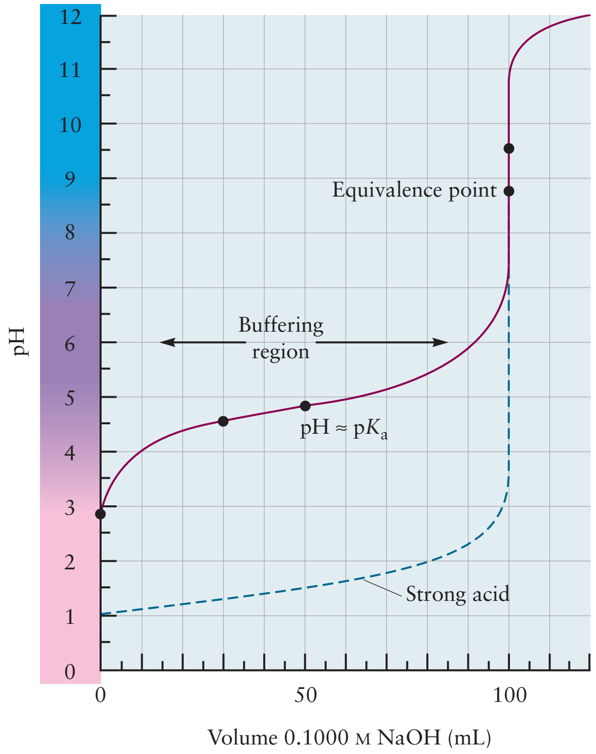


FIGURE 15.14 A titration curve for the titration of a weak acid by a strong base. The curve shown in red is for 100.0 mL of 0.1000 M CH_3COOH titrated with 0.1000 M NaOH. For comparison, the dashed blue line shows the titration curve for a strong acid of the same amount and concentration as presented in Figure 15.13.

There are four distinct ranges in the titration; each corresponds to a type of calculation that we have illustrated already. Figure 15.14 shows pH versus volume for this titration, and the following paragraphs outline the calculation of four typical points on the curve.

1. **$V = 0$ mL NaOH added**
   At the beginning of the titration—before any NaOH is added—the problem is simply the ionization of a weak acid, considered in Section 15.4. A calculation analogous to those of Examples 15.3 and 15.4 gives a pH of 2.88.
2. **$0 < V < V_e$**
   In this range the acid has been partially neutralized by added NaOH solution. Because OH^- is a stronger base than acetate ion, it reacts almost completely with the acid originally present:

$$CH_3COOH(aq) + OH^-(aq) \rightleftharpoons H_2O(\ell) + CH_3COO^-(aq)$$

$$K = \frac{1}{K_b} = \frac{K_a}{K_w} = 2 \times 10^9 \gg 1$$

As a specific example, suppose that 30.00 mL of 0.1000 M NaOH has been added. The 30.00 mL NaOH contains

$$(0.1000 \text{ mol L}^{-1})(0.03000 \text{ L}) = 3.000 \times 10^{-3} \text{ mol OH}^-$$

and the original solution contained

$$(0.1000 \text{ mol L}^{-1})(0.1000 \text{ L}) = 1.000 \times 10^{-2} \text{ mol CH}_3\text{COOH}$$

The neutralization reaction generates one CH_3COO^- ion for every OH^- ion added. Hence, 3.000×10^{-3} mol of CH_3COO^- ions is generated. The amount of acetic acid that remains unreacted is

$$1.000 \times 10^{-2} - 3.000 \times 10^{-3} = 7.00 \times 10^{-3} \text{ mol}$$

Because the total volume is now 130.0 mL (or 0.1300 L), the nominal concentrations after reaction are

$$[\mathrm{CH_3COOH}] \approx \frac{7.00 \times 10^{-3}\ \mathrm{mol}}{0.1300\ \mathrm{L}} = 5.38 \times 10^{-2}\ \mathrm{M}$$

$$[\mathrm{CH_3COO^-}] \approx \frac{3.00 \times 10^{-3}\ \mathrm{mol}}{0.1300\ \mathrm{L}} = 2.31 \times 10^{-2}\ \mathrm{M}$$

This is merely a buffer solution containing acetic acid at a concentration of 5.38×10^{-2} M and sodium acetate at a concentration of 2.31×10^{-2} M. Because the K_a for acetic acid is larger than 10^{-7}, hydronium ion (not hydroxide ion) predominates, and this is an acidic buffer. The pH can be found from the procedure used in Example 15.7 or, more approximately from Equation 15.7

$$\mathrm{pH} \approx \mathrm{p}K_a - \log_{10}\frac{[\mathrm{CH_3COOH}]_0}{[\mathrm{CH_3COO^-}]_0} = 4.75 - \log_{10}\frac{5.38 \times 10^{-2}}{2.31 \times 10^{-2}} = 4.38$$

This region of the titration shows clearly the buffering action of a mixture of a weak acid with its conjugate base. At the half-equivalence point $V = V_e/2$, $[\mathrm{CH_3COOH}]_0 = [\mathrm{CH_3COO^-}]_0$, which corresponds to an equimolar buffer; at this point $\mathrm{pH} \approx \mathrm{p}K_a$. On either side of this point the pH rises relatively slowly as the NaOH solution is added.

3. $V = V_e$

At the equivalence point, $c_t V_e$ mol of $\mathrm{OH^-}$ has been added to the same number of moles of $\mathrm{CH_3COOH}$. An identical solution could have been prepared simply by adding $c_t V_e = 1.000 \times 10^{-2}$ mol of the base $\mathrm{CH_3COO^-}$ (in the form of $\mathrm{NaCH_3COO}$) to 0.2000 L of water. The pH at the equivalence point corresponds to the hydrolysis of $\mathrm{CH_3COO^-}$:

$$\mathrm{H_2O}(\ell) + \mathrm{CH_3COO^-}(aq) \rightleftharpoons \mathrm{CH_3COOH}(aq) + \mathrm{OH^-}(aq)$$

as considered in Example 15.6. At the equivalence point the pH is 8.73.

Note that in the titration of a weak acid by a strong base the equivalence point comes not at pH 7 but at a higher (more basic) value. By the same token, the equivalence point in the titration of a weak base by a strong acid occurs at a pH lower than 7.

4. $V > V_e$

Beyond the equivalence point, $\mathrm{OH^-}(aq)$ is added to a solution of the base $\mathrm{CH_3COO^-}$. The $[\mathrm{OH^-}]$ comes almost entirely from the hydroxide ion added beyond the equivalence point; very little comes from the reaction of the $\mathrm{CH_3COO^-}$ with water. Beyond V_e, the pH for the titration of a weak acid by a strong base is very close to that for a strong acid by a strong base.

The equivalent volume V_e is readily determined in the laboratory by using an indicator that changes color near pH 8.7, the pH at the equivalence point of the acetic acid titration. A suitable choice would be phenolphthalein, which changes from colorless to red over a pH range from 8.2 to 10.0. The slope of pH versus volume of strong base is less steep near the equivalence point for a weak acid than it is for a strong acid, so determination of the equivalent volume—and of the unknown weak acid concentration—is somewhat less accurate.

The following example shows how to determine concentrations and ionization constants for unknown acids and bases from titrations.

EXAMPLE 15.11

A volume of 50.00 mL of a weak acid of unknown concentration is titrated with a 0.1000 M solution of NaOH. The equivalence point is reached after 39.30 mL of NaOH solution has been added. At the half-equivalence point (19.65 mL) the pH is 4.85. Calculate the original concentration of the acid and its ionization constant K_a.

SOLUTION

The number of moles of acid originally present, $c_0 V_0$, is equal to the number of moles of base added at the equivalence point, $c_t V_e$, so

$$c_0 = \frac{V_e}{V_0} c_t = \frac{39.50 \text{ mL}}{50.00 \text{ mL}} \times 0.100 \text{ M} = .0786 \text{ M}$$

This is the original concentration of acid.

At the half-equivalence point,

$$\text{pH} = 4.85 \approx \text{p}K_a$$

$$K_a = 10^{-4.85} = 1.4 \times 10^{-5}$$

The unknown acid could be propionic acid, CH_3CH_2COOH (see Table 15.2).

Related Problems: 61, 62

15.7 Polyprotic Acids

So far, we have considered only **monoprotic acids,** whose molecules can donate only a single hydrogen ion to acceptor molecules. **Polyprotic acids** can donate two or more hydrogen ions to acceptors. Sulfuric acid is a familiar and important example. It reacts in two stages; first

$$H_2SO_4(aq) + H_2O(\ell) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$$

to give the hydrogen sulfate ion, and then

$$HSO_4^-(aq) + H_2O(\ell) \longrightarrow H_3O^+(aq) + SO_4^{2-}(aq)$$

The hydrogen sulfate ion is amphoteric, meaning that it is a base in the first reaction (with conjugate acid H_2SO_4) and an acid in the second (with conjugate base SO_4^{2-}). In its first ionization H_2SO_4 is a strong acid, but the product of that ionization (HSO_4^-) is a weak acid. So, the H_3O^+ produced in a solution of H_2SO_4 comes primarily from the first ionization, and the solution has a pH close to that of a monoprotic strong acid of the same concentration. But when this solution reacts with a strong base, its neutralizing power is twice that of a monoprotic acid of the same concentration, because each mole of sulfuric acid can react with and neutralize two moles of hydroxide ion.

Weak Polyprotic Acids

Weak polyprotic acids ionize in two or more stages. Examples are carbonic acid (H_2CO_3), formed from solvated CO_2 (carbonated water; Fig. 15.15), and phosphoric acid (H_3PO_4). Carbonic acid can give up one hydrogen ion to form HCO_3^- (hydrogen carbonate ion) or two hydrogen ions to form CO_3^{2-} (carbonate ion). Phosphoric acid ionizes in three stages, giving successively $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}.

Two simultaneous equilibria are involved in the ionization of a diprotic acid such as H_2CO_3:[2]

$$H_2CO_3(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

$$\frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = K_{a1} = 4.3 \times 10^{-7}$$


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FIGURE 15.15 The indicator phenolphthalein is pink in basic solution *(left).* When dry ice (solid carbon dioxide) is placed in the bottom of the beaker *(right),* it dissolves to form carbonic acid. This neutralizes the base in solution, and causes the indicator to change to its colorless form characteristic of an acid solution.

---

[2] An accurate description of carbonic acid and solvated CO_2 is somewhat more complicated than indicated here. In fact, most of the dissolved CO_2 remains as $CO_2(aq)$, and only a small fraction actually reacts with water to give $H_2CO_3(aq)$. However, we will indicate by $[H_2CO_3]$ the total concentration of both of these species. Approximately 0.034 mol of CO_2 dissolves per liter of water at 25°C and atmospheric pressure.

and

$$HCO_3^-(aq) + H_2O(\ell) \rightleftarrows H_3O^+(aq) + CO_3^{2-}(aq)$$

$$\frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = K_{a2} = 4.8 \times 10^{-11}$$

We emphasize two important points at the outset:

1. The $[H_3O^+]$ in the two ionization equilibria are one and the same.
2. K_{a2} is invariably smaller than K_{a1} because the negative charge left behind by the loss of a hydrogen ion in the first ionization causes the second hydrogen ion to be more tightly bound.

Exact calculations of simultaneous equilibria can be complicated. They simplify considerably when the original acid concentration is not too small and the ionization constants K_{a1} and K_{a2} differ substantially in magnitude (by a factor of 100 or more). The latter condition is almost always satisfied. Under such conditions, the two equilibria can be treated sequentially, as in the following example.

EXAMPLE 15.12

Calculate the equilibrium concentrations of H_2CO_3, HCO_3^-, CO_3^{2-}, and H_3O^+ in a saturated aqueous solution of CO_2, in which the original concentration of H_2CO_3 is 0.034 M.

SOLUTION

The H_3O^+ arises both from the ionization of H_2CO_3 and from the subsequent ionization of HCO_3^-, but because $K_{a1} \gg K_{a2}$ it is reasonable to ignore the contribution of $[H_3O^+]$ from the second ionization (as well as from the autoionization of water). These approximations will be checked later in the calculation.

If y mol L^{-1} of H_2CO_3 ionizes, the following approximations apply:

	$H_2CO_3(aq)$ + $H_2O(\ell)$ $\rightleftarrows$	$H_3O^+(aq)$ +	$HCO_3^-(aq)$
Initial concentration (M)	0.034	≈0	0
Change in concentration (M)	$-y$	$+y$	$+y$
Equilibrium concentration (M)	$0.034 - y$	y	y

where equating both $[HCO_3^-]$ and $[H_3O^+]$ to y involves the assumption that the subsequent ionization of HCO_3^- has only a small effect on its concentration. Then the first ionization equilibrium can be written as

$$\frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = K_{a1}$$

$$\frac{y^2}{0.034 - y} = 4.3 \times 10^{-7}$$

Solving this equation for y gives

$$y = 1.2 \times 10^{-4} \text{ M} = [H_3O^+] = [HCO_3^-]$$

$$[H_2CO_3] = 0.034 - y = 0.034 \text{ M}$$

The second equilibrium can be written as

$$\frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = K_{a2} = \frac{(1.2 \times 10^{-4})[CO_3^{2-}]}{1.2 \times 10^{-4}} = 4.8 \times 10^{-11}$$

$$[CO_3^{2-}] = 4.8 \times 10^{-11} \text{ M}$$

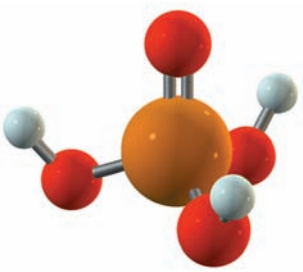
The concentration of the base produced in the second ionization, $[CO_3^{2-}]$, is numerically equal to K_{a2}.

Now we must check the validity of the assumptions. Because

$$[CO_3^{2-}] = 4.8 \times 10^{-11}\ \text{M} \ll 1.2 \times 10^{-4}\ \text{M} = [HCO_3^-]$$

we were justified in ignoring the effect of the second ionization on the concentrations of HCO_3^- and H_3O^+. The additional concentration of H_3O^+ furnished by HCO_3^- is only 4.8×10^{-11} M. Finally, $[H_3O^+]$ is much larger than 10^{-7} M, so neglecting the water autoionization was also justified.

Related Problems: 63, 64



Phosphoric acid, H_3PO_4, is a triprotic acid that is used in the manufacture of phosphate fertilizers and in the food industry.

For a triprotic acid such as H_3PO_4, the concentration of the base (PO_4^{3-}) resulting from the third ionization could have been calculated in a similar manner.

An analogous procedure applies to the reactions of a base that can accept two or more hydrogen ions. In a solution of sodium carbonate (Na_2CO_3), the carbonate ion reacts with water to form first HCO_3^- and then H_2CO_3:

$$H_2O(\ell) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

$$\frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]} = K_{b1} = \frac{K_w}{K_{a2}} = 2.1 \times 10^{-4}$$

$$H_2O(\ell) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

$$\frac{[OH^-][H_2CO_3]}{[HCO_3^-]} = K_{b2} = \frac{K_w}{K_{a1}} = 2.3 \times 10^{-8}$$

In this case $K_{b1} \gg K_{b2}$, so essentially all the OH^- arises from the first reaction.

The ensuing calculation of the concentrations of species present is just like that in Example 15.12.

Effect of pH on Solution Composition

Changing the pH of a solution shifts the positions of all acid–base equilibria, including those involving polyprotic acids. Acid–base equilibrium expressions and equilibrium constants are used to calculate the amount of the change. For example, the two equilibria that apply to solutions containing H_2CO_3, HCO_3^-, and CO_3^{2-} can be written as

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_{a1}}{[H_3O^+]} \qquad \frac{[CO_3^{2-}]}{[HCO_3^-]} = \frac{K_{a2}}{[H_3O^+]}$$

At a given pH, the right sides are known and the relative amounts of the three carbonate species can be calculated. This is illustrated by the following example.

EXAMPLE 15.13

Calculate the fraction of carbonate present as H_2CO_3, HCO_3^-, and CO_3^{2-} at pH 10.00.

SOLUTION

At this pH, $[H_3O^+] = 1.0 \times 10^{-10}$ M, and the values of K_{a1} and K_{a2} for the preceding equations are used to find

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{4.3 \times 10^{-7}}{1.0 \times 10^{-10}} = 4.3 \times 10^3$$

$$\frac{[CO_3^{2-}]}{[HCO_3^-]} = \frac{4.8 \times 10^{-11}}{1.0 \times 10^{-10}} = 0.48$$

It is most convenient to rewrite these ratios with the same species (say, HCO_3^-) in the denominator. The first equation becomes

$$\frac{[H_2CO_3]}{[HCO_3^-]} = \frac{1}{4.3 \times 10^3} = 2.3 \times 10^{-4}$$

The fraction of each species present is obtained by dividing the concentration of each species by the sum of the three concentrations. For H_2CO_3 this gives

$$\text{fraction } H_2CO_3 = \frac{[H_2CO_3]}{[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]}$$

This can be simplified by dividing numerator and denominator by $[HCO_3^-]$ and substituting the ratios that have already been calculated:

$$\text{fraction } H_2CO_3 = \frac{[H_2CO_3]/[HCO_3^-]}{([H_2CO_3]/[HCO_3^-]) + 1 + ([CO_3^{2-}]/[HCO_3^-])}$$

$$= \frac{2.3 \times 10^{-4}}{2.3 \times 10^{-4} + 1 + 0.48} = 1.6 \times 10^{-4}$$

In the same way the fractions of HCO_3^- and CO_3^{2-} present are calculated to be 0.68 and 0.32, respectively.

Related Problems: 67, 68

Repeating the calculation of Example 15.13 at a series of different pH values gives the graph shown in Figure 15.16. At high pH, CO_3^{2-} predominates, and at low pH, H_2CO_3 is the major species. At intermediate pH (near pH 8, the approximate pH of seawater), the hydrogen carbonate ion HCO_3^- is most prevalent. The variation in composition of sedimentary rocks from different locations can be traced back to the effect of pH on solution composition. Sediments containing carbonates were formed from alkaline (high-pH) lakes and oceans in which CO_2 was present mainly as CO_3^{2-} ion. Sediments deposited from waters with intermediate pH are hydrogen carbonates or mixtures between carbonates and hydrogen carbonates. An example of the latter is trona ($2Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), an ore from the western United States that is an important source of both carbonates of sodium. Acidic waters did not deposit carbonates, but instead released $CO_2(g)$ to the atmosphere.

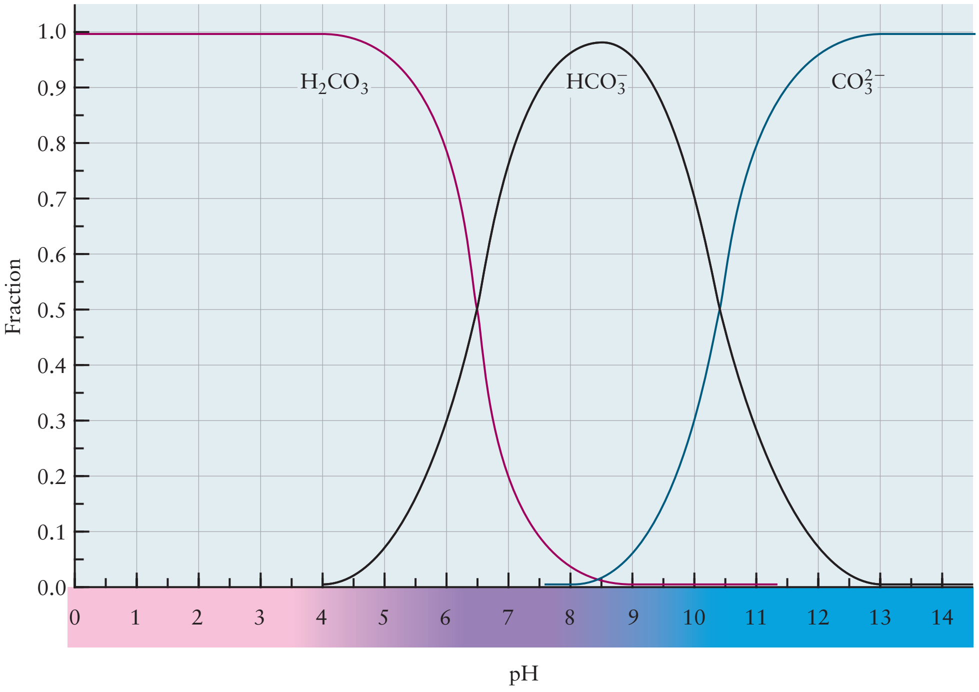


FIGURE 15.16 The equilibrium fractions of H_2CO_3, HCO_3^-, and CO_3^{2-} that are present in aqueous solution at different values of the pH.

A DEEPER LOOK

15.8 Exact Treatment of Acid–Base Equilibria

Sections 15.4 and 15.5 outline methods for calculating equilibria involving weak acids, bases, and buffer solutions. There we assume that the amount of hydronium ion (or hydroxide ion) resulting from the ionization of water can be neglected in comparison with that produced by the ionization of dissolved acids or bases. In this section, we replace that approximation by a treatment of acid–base equilibria that is exact, within the limits of the mass-action law. This approach leads to somewhat more complicated equations, but it serves several purposes. It has great practical importance in cases in which the previous approximations no longer hold, such as very weak acids or bases or very dilute solutions. It includes as special cases the various aspects of acid–base equilibrium considered earlier. Finally, it provides a foundation for treating amphoteric equilibrium later in this section.

Consider a general case in which the initial concentration of a weak acid HA is called c_a, and the initial concentration of its conjugate base (which for simplicity is assumed to come from the salt NaA) is c_b. In solution there will be five dissolved species: HA, A^-, Na^+, H_3O^+, and OH^-. It is necessary to write down and solve five independent equations that relate the equilibrium concentrations of these species to the initial concentrations c_a and c_b and to K_a, the acid ionization constant of HA. The first equation is simply

$$[Na^+] = c_b \tag{a}$$

reflecting the fact that the $Na^+(aq)$ from the dissolved salt is a spectator ion that does not take part in the acid–base equilibrium. Next there are two equilibrium relations:

$$[H_3O^+][OH^-] = K_w \tag{b}$$

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

The fourth relation is one of stoichiometry, or conservation of "A-material":

$$c_a + c_b = [HA] + [A^-] \tag{d}$$

The original A-material was introduced either as acid or as base, with a total concentration of $c_a + c_b$. When equilibrium is reached, some redistribution has doubtless occurred, but the *total* concentration, $[HA] + [A^-]$, must be the same. The fifth and final relation results from charge balance. The solution must be electrically neutral, so the total amount of positive charge must be equal to the total amount of negative charge:

$$[Na^+] + [H_3O^+] = [A^-] + [OH^-] \tag{e}$$

These five independent equations completely determine the five unknown concentrations. To solve them, begin by substituting (a) into (e) and solving for $[A^-]$:

$$[A^-] = c_b + [H_3O^+] - [OH^-] \tag{e$'$}$$

Next, insert (e′) into (d) and solve for [HA]:

$$[HA] = c_a + c_b - [A^-] = c_a - [H_3O^+] + [OH^-] \tag{d$'$}$$

Next, substitute both (d′) and (e′) into (c) to find

$$\frac{[H_3O^+](c_b + [H_3O^+] - [OH^-])}{(c_a - [H_3O^+] + [OH^-])} = K_a \tag{c$'$}$$

There are two ways to proceed with the general equation (c′). First, we can set up the exact solution for $[H_3O^+]$, a procedure that is useful for very weak acids or bases or for very dilute solutions. Or, we can reduce (c′) in various limits to cases already considered.

For the exact solution, eliminate $[OH^-]$ in (c′) by using (b). This gives

$$\frac{[H_3O^+]\left(c_b + [H_3O^+] - \dfrac{K_w}{[H_3O^+]}\right)}{\left(c_a - [H_3O^+] + \dfrac{K_w}{[H_3O^+]}\right)} = K_a$$

The numerator and denominator are multiplied by $[H_3O^+]$ and the fraction is cleared by moving the denominator to the right side:

$$[H_3O^+](c_b[H_3O^+] + [H_3O^+]^2 - K_w) = K_a(c_a[H_3O^+] - [H_3O^+]^2 + K_w)$$

This can be rewritten as

$$[H_3O^+]^3 + (c_b + K_a)[H_3O^+]^2 - (K_w + c_aK_a)[H_3O^+] - K_aK_w = 0$$

This is a cubic equation for $[H_3O^+]$, which can be solved with a calculator. The concentrations of OH^-, A^-, and HA can then be found by successive substitutions into (b), (e′), and (d′).

Alternatively, the general equation (c′) can be examined in various limits. In an acidic buffer (as in Examples 15.7 and 15.8), if it can be assumed that $[H_3O^+] \gg [OH^-]$, then (c′) simplifies to

$$\frac{[H_3O^+](c_b + [H_3O^+])}{(c_a - [H_3O^+])} = K_a$$

which is exactly the equation used in those examples. If, in addition, $c_b = 0$, the weak-acid ionization limit of Examples 15.3 and 15.4 is reached. In a basic buffer, if it can be assumed that $[OH^-] \gg [H_3O^+]$, then (c′) simplifies to

$$\frac{(K_w/[OH^-])(c_b - [OH^-])}{(c_a + [OH^-])} = K_a$$

Here (b) was used to substitute for $[H_3O^+]$ where it multiplies the whole expression. This can be rewritten as

$$\frac{[OH^-](c_a + [OH^-])}{(c_b - [OH^-])} = \frac{K_w}{K_a} = K_b$$

which is exactly the equation used in Example 15.9. If no acid is present initially ($c_a = 0$), this expression reduces to the weak-base ionization limits of Examples 15.5 and 15.6. The general approach includes all of the previous calculations as special cases.

Unless conditions require the use of the exact solution, approximate equations are preferable because they are easier to apply and provide greater physical insight. If a calculation (ignoring water autoionization) of the ionization of a weak acid gives a concentration of H_3O^+ smaller than 10^{-6} M or if a calculation of base ionization gives a concentration of OH^- smaller than 10^{-6} M, then we have to use the more exact treatment. For buffer solutions, a pH near 7 does not necessarily mean that water ionization is important, unless the acid or base concentration becomes very small.

EXAMPLE 15.14

Calculate the pH of a 1.00×10^{-5} M solution of HCN(*aq*). The K_a of HCN(*aq*) is 6.17×10^{-10}.

SOLUTION

Suppose the autoionization of water is ignored and the method of Examples 15.3 and 15.4 is used. This gives $[H_3O^+] = 7.9 \times 10^{-8}$ M, which of course makes no sense, because it is *lower* than the concentration of hydronium ion in pure water. HCN is a very weak acid, but it is nonetheless an acid, not a base.

So, we have to use the exact cubic equation for $[H_3O^+]$, inserting into it the proper coefficients and taking $c_a = 1.00 \times 10^{-5}$ and $c_b = 0$. This gives

$$[H_3O^+]^3 + 6.17 \times 10^{-10}[H_3O^+]^2 - 1.617 \times 10^{-14}[H_3O^+] - 6.17 \times 10^{-24} = 0$$

Unfortunately, there is no method as simple as the quadratic formula to solve a cubic equation. The easiest way to solve this equation is to try a series of values for $[H_3O^+]$ on the left side, varying them to obtain a result as close as possible to 0 (see Appendix C). It is safe to assume that the final answer will be slightly larger than 1×10^{-7}, so the initial guesses should be of that magnitude. Carrying out the procedure gives

$$[H_3O^+] = 1.27 \times 10^{-7}\ \text{M} \qquad \text{pH} = 6.90$$

Related Problems: 69, 70

Amphoteric Equilibria

A second situation in which an exact analysis of acid–base equilibrium is useful occurs when an amphoteric species is dissolved in water. The hydrogen carbonate ion (HCO_3^-) is amphoteric because it can act as an acid in the equilibrium

$$HCO_3^-(aq) + H_2O(\ell) \rightleftarrows H_3O^+(aq) + CO_3^{2-}(aq)$$

$$\frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = K_{a2} = 4.8 \times 10^{-11}$$

or as a base in the equilibrium

$$H_2O(\ell) + HCO_3^-(aq) \rightleftarrows H_2CO_3(aq) + OH^-(aq)$$

$$\frac{[OH^-][H_2CO_3]}{[HCO_3^-]} = K_{b2} = 2.3 \times 10^{-8}$$

If sodium hydrogen carbonate ($NaHCO_3$) is dissolved in water, there is a competition between the tendency of HCO_3^- to accept hydrogen ions and to donate them. Because $K_{b2} > K_{a2}$, there should be more production of OH^- than of H_3O^+, so the solution should be basic.

In an exact treatment of this equilibrium, there are six unknown concentrations—those of Na^+, H_2CO_3, HCO_3^-, CO_3^{2-}, OH^-, and H_3O^+. Two equilibrium equations were already presented, and a third relates $[OH^-]$ and $[H_3O^+]$ to K_w. If $[HCO_3^-]_0$ is the original concentration of $NaHCO_3$, then from stoichiometry

$$[HCO_3^-]_0 = [HCO_3^-] + [H_2CO_3] + [CO_3^{2-}]$$

because the total amount of carbonate material is conserved. Any reduction in $[HCO_3^-]$ must be compensated by a corresponding increase in either $[H_2CO_3]$ or $[CO_3^{2-}]$. Next we use the principle of conservation of charge. The positively charged species present are Na^+ and H_3O^+, and the negatively charged species are HCO_3^-, CO_3^{2-}, and OH^-. Because there is overall charge neutrality,

$$[Na^+] + [H_3O^+] = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-]$$

where the coefficient 2 for $[CO_3^{2-}]$ arises because each carbonate ion is doubly charged. In addition, the Na^+ concentration is unchanged, so

$$[Na^+] = [HCO_3^-]_0$$

In principle, these six equations can be solved simultaneously to calculate the exact $[H_3O^+]$ for an arbitrary initial concentration of HCO_3^-. The result is complex and gives little physical insight. Instead, we give only a simpler, approximate solution, which is sufficient in the cases considered here. Subtracting the carbonate balance equation from the charge balance equation gives

$$[H_3O^+] = [CO_3^{2-}] - [H_2CO_3] + [OH^-]$$

The three equilibrium expressions are used to rewrite this as

$$[H_3O^+] = K_{a2}\frac{[HCO_3^-]}{[H_3O^+]} - \frac{[H_3O^+][HCO_3^-]}{K_{a1}} + \frac{K_w}{[H_3O^+]}$$

where $[CO_3^{2-}]$ and $[H_2CO_3]$ have been eliminated in favor of $[HCO_3^-]$.

Multiplying by $K_{a1}[H_3O^+]$ gives

$$K_{a1}[H_3O^+]^2 + [HCO_3^-][H_3O^+]^2 = K_{a1}K_{a2}[HCO_3^-] + K_{a1}K_w$$

$$[H_3O^+]^2 = \frac{K_{a1}K_{a2}[HCO_3^-] + K_{a1}K_w}{K_{a1} + [HCO_3^-]}$$

This equation still contains two unknown quantities, $[H_3O^+]$ and $[HCO_3^-]$. Because both K_{a2} and K_{b2} are small, $[HCO_3^-]$ should be close to its original value, $[HCO_3^-]_0$. If $[HCO_3^-]$ is set equal to $[HCO_3^-]_0$, this becomes

$$[H_3O^+]^2 \approx \frac{K_{a1}K_{a2}[HCO_3^-]_0 + K_{a1}K_w}{K_{a1} + [HCO_3^-]_0}$$

which can be solved for $[H_3O^+]$. In many cases of interest, $[HCO_3^-]_0 \gg K_{a1}$, and $K_{a2}\,[HCO_3^-]_0 \gg K_w$. When this is so, the expression simplifies to

$$[H_3O^+]^2 \approx K_{a1}K_{a2}$$

$$[H_3O^+] \approx \sqrt{K_{a1}K_{a2}}$$

$$\text{pH} \approx \frac{1}{2}(\text{p}K_{a1} + \text{p}K_{a2})$$

so the pH of such a solution is the average of the pK_a values for the two ionizations.

EXAMPLE 15.15

What is the pH of a solution that is 0.100 M in $NaHCO_3$?

SOLUTION

First, the two assumptions are checked:

$$[HCO_3^-]_0 = 0.100 \gg 4.3 \times 10^{-7} = K_{a1}$$

$$[HCO_3^-]_0 K_{a2} = 4.8 \times 10^{-12} \gg 1.0 \times 10^{-14} = K_w$$

so both are satisfied. Therefore,

$$[H_3O^+] = \sqrt{K_{a1}K_{a2}} = 4.5 \times 10^{-9}\ \text{M}$$

$$\text{pH} = 8.34$$

and the solution is basic, as expected.

Titration of a Polyprotic Acid

A polyprotic acid has more than one equivalence point. The first equivalence point occurs when the volume V_{e1} of base added is sufficient to remove one hydrogen ion from each acid molecule, V_{e2} is the volume sufficient to remove two hydrogen ions from each, and so forth. A diprotic acid shows two equivalence points, and a triprotic acid, three. The equivalent volumes are related to each other by

$$V_{e1} = \frac{1}{2} V_{e2} = \frac{1}{3} V_{e3}$$

Figure 15.17 shows a titration curve for triprotic phosphoric acid. The three equivalence points are at 100.0 mL, 200.0 mL, and 300.0 mL. Calculating the pH as a function of the volume of added base presents no new complications beyond those already considered. The initial pH is given by a calculation analogous to that of Example 15.12, and the pH in the flat regions between equivalence points is obtained by a buffer calculation like that for a diprotic acid. For example, the pH after addition of 50.0 mL of base is that of an equimolar $H_3PO_4/H_2PO_4^-$ buffer (subsequent ionization of $H_2PO_4^-$ can be ignored). Finally, the pH at the first equivalence point is that for a solution of NaH_2PO_4 and uses the amphoteric equilibria equations presented earlier in this section (PO_4^{3-} can be ignored in this case). The pH at the second equivalence point is an amphoteric equilibrium in which HPO_4^{2-} is in equilibrium with $H_2PO_4^-$ and with PO_4^{3-}.

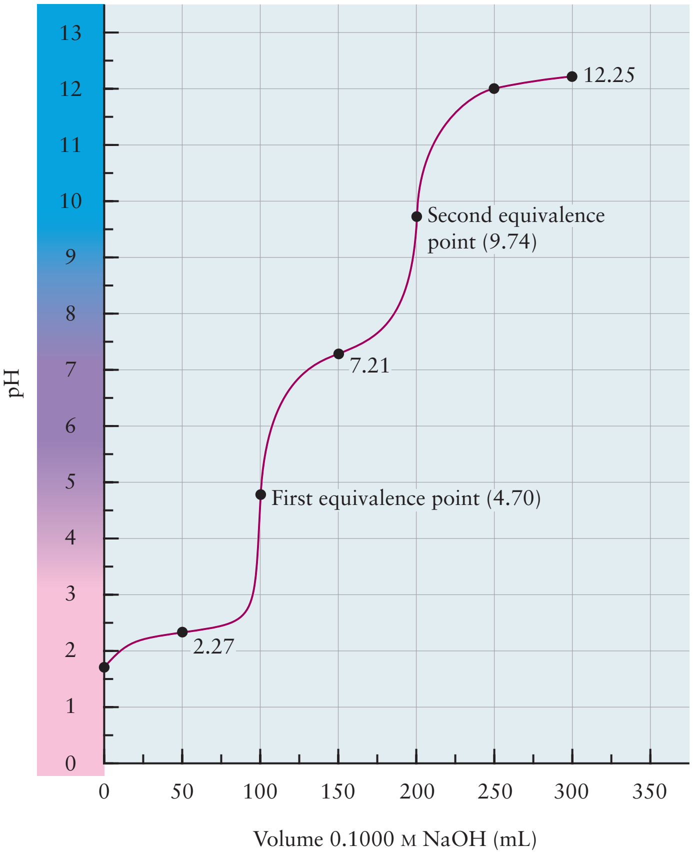


FIGURE 15.17 A titration curve for the titration of a polyprotic acid (phosphoric acid) by a strong base. The curve shown is for 100.0 mL of 0.1000 M H_3PO_4 titrated with 0.1000 M NaOH. No clear third equivalence point is seen at 300 mL because K_a for HPO_4^{2-} is not much greater than K_a for H_2O in aqueous solution.

15.9 Organic Acids and Bases: Structure and Reactivity

One of the goals of organic chemistry is to understand the relationship between *structure* and *function*. How does the molecular structure of an organic compound (including its attached functional groups) affect its chemical reactivity? As an example of the exploration of structure–function relationships we consider here the trends in acid strength in organic compounds. This extends the earlier discussion of acid strength in inorganic acids (see Section 15.3) and illustrates the usefulness of chemical concepts such as electronegativity and resonance in predicting reactivity. This section depends on the thermodynamic description in Section 14.3.

Table 15.2 lists a number of organic acids with pK_a values in aqueous solution between 0 (strong acid) and 14 (weak acid). Almost all of them are carboxylic acids with the characteristic —COOH functional group. Acid ionization constants can be also defined for many other functional groups besides carboxylic acids. They provide important information about reactivity, because many organic reactions involve the transfer of hydrogen ions or catalysis by acids or bases.

Aqueous solutions can be used to describe acidity only in compounds with values of the pK_a between about 14 and 0. Values much greater than 14 mean that there is negligible ionization in aqueous solution, and values much less than 0 mean that ionization is essentially complete. Because our goal is a scale of *relative* acidities, we can use information from nonaqueous solvents. In a sufficiently basic solvent, even a very weak acid will show some ionization; in a sufficiently acidic solvent, even a very strong acid will be only partially ionized. This allows an extension of the pK_a scale above 14 and below 0, provided we consistently think of it as only a relative scale. We thus generalize our earlier definition of K_a, which was limited to aqueous solvents, to describe acid ionization in a general solvent:

$$\text{HA} + \text{solvent} \rightleftharpoons \text{solvent-H}^+ + \text{A}^-$$

Our assumption is that the *difference* in pK_a values for two different acids in a given solvent

$$\text{p}K_a - \text{p}K'_a = -\log_{10}(K_a/K'_a)$$

depends only weakly on the particular solvent chosen, even though the actual pK_a values are very sensitive to the solvent. If this is the case, we can extend the pK_a scale beyond the range that comes from measurements of pH in aqueous solution. The result is given in Table 15.4.

A thermodynamic analysis shows that this difference in pK_a values is related to the difference in the standard Gibbs free energy changes for the two reactions:

$$\Delta G° - \Delta G°' = -RT(\ln K_a - \ln K'_a) = 2.3\, RT(\text{p}K_a - \text{p}K'_a) \qquad [15.8]$$

The factor 2.3 appears when we relate the natural logarithm to the base 10 logarithm. The difference in standard Gibbs free energy changes can be separated into one contribution arising from standard enthalpy changes and one from absolute entropy changes:

$$\Delta G° - \Delta G°' = \Delta H° - \Delta H°' - T(\Delta S° - \Delta S°')$$

If we change the structure of an organic acid, what will be the effect on the pK_a? In general, modest structural changes such as the replacement of a functional group have only small effects on the entropy change of ionization, and most of the influence comes through changes in the enthalpy change of ionization. The quantitative magnitude of this effect is calculated in the following example.

EXAMPLE 15.16

How large a change in energy (or enthalpy) of reaction is needed for an acid ionization to lower the pK_a by one unit at 25°C? Assume that the entropy of ionization is unchanged.

SOLUTION

The entropy of ionization is unchanged, so $\Delta S° = \Delta S°'$, and $\Delta H° - \Delta H°' = \Delta G° - \Delta G°'$. If the change in p$K_a$ is 1.00, then the change in Gibbs free energy must be

$$\Delta G° - \Delta G°' = -RT(\ln K_a - \ln K'_a) = 2.3\, RT(\text{p}K_a - \text{p}K'_a) = 2.3\, RT(-1)$$

$$= 2.3(8.315 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})(-1) = -5700 \text{ J mol}^{-1} = -5.7 \text{ kJ mol}^{-1}$$

If we assume that this change in Gibbs free energy is entirely due to a change in enthalpy, then one unit of pK_a change corresponds to a lowering of the enthalpy of the products relative to the reactants by 5.7 kJ mol^{-1}.

Related Problems: 73, 74

TABLE 15.4 Acidities of Organic Compounds

Acid	pK_a	Conjugate Base
$CH_3{-}CH_3$	50	$CH_3{-}\ddot{C}H_2^-$
CH_4	49	$:CH_3^-$
$CH_2{=}CH_2$	44	$CH_2{=}\ddot{C}H^-$
C_6H_6	43	$C_6H_5^-$
$C_6H_5CH_3$	41	$C_6H_5\ddot{C}H_2^-$
$CH_3CH_2NH_3^+$	35	$CH_3CH_2NH_2$
$(C_6H_5)_3CH$	32	$(C_6H_5)_3\ddot{C}^-$
$HC{\equiv}CH$	25	$HC{\equiv}\ddot{C}^-$
CH_3COCH_3	20	$CH_3CO\ddot{C}H_2^-$
$(CH_3)_3C\ddot{\underset{\cdot\cdot}{O}}H$	18	$(CH_3)_3C\ddot{\underset{\cdot\cdot}{O}}:^-$
$C_2H_5\ddot{\underset{\cdot\cdot}{O}}H$	16	$C_2H_5\ddot{\underset{\cdot\cdot}{O}}:^-$
$H_2\ddot{\underset{\cdot\cdot}{O}}$	15.7	$H\ddot{\underset{\cdot\cdot}{O}}:^-$
$CH_3\ddot{O}H$	15	$CH_3\ddot{\underset{\cdot\cdot}{O}}:^-$
$(NC)_2CH_2$	11.2	$(NC)_2\ddot{C}H^-$
CH_3NO_2	10.2	$:CH_2NO_2^-$
$C_6H_5\ddot{\underset{\cdot\cdot}{O}}H$	10.0	$C_6H_5\ddot{\underset{\cdot\cdot}{O}}:^-$
HCN	9.1	$:CN^-$
$(CH_3CO)_3CH$	5.9	$(CH_3CO)_3\ddot{C}^-$
CH_3CO_2H	4.8	$CH_3CO_2^-$
$C_6H_5CO_2H$	4.2	$C_6H_5CO_2^-$
HCO_2H	3.7	HCO_2^-
$CH_2(NO_2)_2$	3.6	$:CH(NO_2)_2^-$
$ClCH_2CO_2H$	2.9	$ClCH_2CO_2^-$
Cl_2CHCO_2H	1.3	$Cl_2CHCO_2^-$
Cl_3CCO_2H	0.7	$Cl_3CCO_2^-$
$CH_3CONH_3^+$	0.3	$CH_3CO\dot{N}H_2$
HNO_3	−1.4	NO_3^-
H_3O^+	−1.7	H_2O
$CH_3\ddot{O}H_2^+$	−2.2	$CH_3\ddot{\underset{\cdot\cdot}{O}}H$
$C_2H_5\ddot{O}H_2^+$	−2.4	$C_2H_5\ddot{\underset{\cdot\cdot}{O}}H$
$(CH_3)_3C\ddot{O}H_2^+$	−3.8	$(CH_3)_3C\ddot{\underset{\cdot\cdot}{O}}H$
$C_6H_5\ddot{O}H_2^+$	−6.7	$C_6H_5\ddot{\underset{\cdot\cdot}{O}}H$
$(CH_3)_2C{=}\ddot{O}H^+$	−7.2	$(CH_3)_2C{=}\ddot{\underset{\cdot\cdot}{O}}$
$R{-}C{\equiv}NH^+$	∼−10	$R{-}C{\equiv}N:$

The sign of the effect is clear from Example 15.16: If a change in structure of a molecule lowers its pK_a (making it a stronger acid), then the energy change for the acid ionization must be lowered. Another way to say this is that the effect of the structural change is to lower the energy of the conjugate base relative to that of the original acid.

An exploration of structure–function relations that lie behind the data in Table 15.4 must examine the effects of changes in molecular structure on the relative energetic stability of acid and conjugate base. We discuss three effects in turn: electronegativity, steric hindrance, and resonance.

Electronegativity

In Section 15.3 (see Fig. 15.6), we pointed out that in inorganic oxoacids with structures $-X-O-H$, the more electronegative the atom X, the more readily the $O^- - H^+$ bond breaks and the stronger the acid. A parallel effect of electronegativity explains the relative acid strengths of hydrocarbons, amines, and alcohols. Table 15.4 shows that ethane, C_2H_6, has a pK_a of 50, whereas that for ethylamine, $C_2H_5NH_2$, is 35 and that for ethanol, C_2H_5OH, is 16. These large changes occur because as the electronegativity increases from carbon to nitrogen to oxygen, the $-X^-$ conjugate base becomes more and more stable and thus the corresponding acid becomes stronger.

A similar situation occurs when electronegative atoms are substituted somewhat farther from the site where ionization takes place. Compare the acid strengths of acetic acid, CH_3COOH, with chloroacetic acid, $ClCH_2COOH$. The electronegative chlorine atom stabilizes the net negative charge of the conjugate base more strongly than does the hydrogen atom in acetic acid, reducing the pK_a from 4.8 to 2.9. Another way to describe this result is as an "inductive" effect involving bond dipoles. The negative charge on the chlorine atom in the Cl—C bond (and the corresponding positive charge on the carbon atom) interact favorably with the negative charge on the $-COO^-$ group of the conjugate base through a dipole-charge interaction (see Section 10.3), stabilizing the base and making the acid stronger:

$$Cl^{\delta-}-C^{\delta+}H_2-COO^-$$

As the substituted electronegative atom moves farther from the site of ionization, its effect on acid strength decreases. Thus, 4-chlorobutanoic acid, $ClCH_2CH_2CH_2COOH$, is a weaker acid (pK_a = 4.5) than 2-chlorobutanoic acid, $CH_3CH_2CHClCOOH$ (pK_a = 2.9).

Because most common functional groups in organic chemistry are more electronegative than hydrogen or carbon atoms (with the exception of metal atoms), their substitution tends to make organic acids stronger; the same is true of positively charged substituents. On the other hand, a negatively charged species such as $-COO^-$ interacts unfavorably with the additional negative change on the base and tends to reduce acidity.

EXAMPLE 15.17

Consider the dicarboxylic acid malonic acid, $HOOC-CH_2-COOH$. It ionizes in two stages with pK_a values pK_{a1} and pK_{a2}. How do you predict the magnitudes of these two will compare with the pK_a of acetic acid, CH_3COOH, which is 4.8?

SOLUTION

Malonic acid shows a substitution of a $-COOH$ functional group for one —H atom in acetic acid. Because this carboxylic acid functional group is more electronegative, it should make the compound more acidic, lowering its pK_a relative to acetic acid (measured value: pK_{a1} = 2.8). Once the first dissociation has taken place, however, the attached functional group in comparison with acetic acid is now $-COO^-$. Because this is negatively charged, it interacts unfavorably with the negative charge that results from the second acid ionization, raising the pK_a relative to that of acetic acid (measured value: pK_{a2} = 5.7).

Related Problem: 75

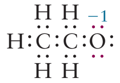
Steric Hindrance

As described in Section 11.2, ions in solution are stabilized through ion–dipole interactions with surrounding solvent molecules. This stabilization is reduced if the charged site is surrounded by bulky groups that prevent solvent molecules from coming close enough. This is an effect of **steric hindrance** on acidity. For example, compare the acidity of methanol, CH_3OH, with *tert*-butanol, $(CH_3)_3COH$. The latter compound is obtained by substituting $-CH_3$ groups for the three $-H$ atoms attached to the carbon atom in methanol. In the corresponding negatively charged conjugate bases CH_3O^- and $(CH_3)_3CO^-$, the former is more stable in solution because solvent molecules can approach the negatively charged site more closely. In the latter, the bulkier —CH_3 groups reduce the stability of the solvated base anion. The net effect is that methanol is a stronger acid in solution ($pK_a = 15$) than *tert*-butanol ($pK_a = 18$).

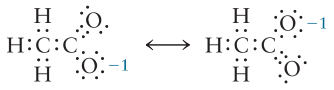
This observation depends on the presence of a liquid solvent around the acid and conjugate base. For the corresponding acid–base pair in the gas phase, *tert*-butanol is a stronger acid than methanol.

Resonance

A third and final contribution to relative acidity of organic compounds is resonance. Let's begin by noting that the acidity of carboxylic acids is considerably greater than that of alcohols. For example, the pK_a of acetic acid, CH_3COOH, is considerably lower than that of ethanol, CH_3CH_2OH (4.8 versus 16). Some of this may be due to the "inductive effect" of substituting an electronegative O atom for two H atoms. But, inductive effects are not typically so large (more than 11 units of pH change). An alternative explanation must be sought, and it can be found in the concept of resonance stabilization, which was introduced in Section 3.8 and discussed in the context of organic molecules in Section 7.8. A single Lewis structure can be drawn for the conjugate base of ethanol:

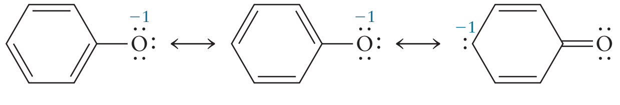


On the other hand, the conjugate base of acetic acid is represented by a resonance hybrid of two Lewis structures:



The existence of more than one resonance structure stabilizes the acetate ion and contributes to the greater acidity of acetic acid.

A second example of resonance stabilization affecting acidity arises in a comparison of phenols and alcohols. Phenol (also called carbolic acid) has a pK_a of 10, whereas the pK_a values for typical alcohols range from 16 to 18. The reason for this difference is the greater stability of the conjugate base (the phenoxide ion, $C_6H_5O^-$) due to the spreading out of the negative charge over the aromatic ring. Several different resonance structures contribute to the stability of the phenoxide ion.



Phenol, although not a strong acid, does react readily with sodium hydroxide to form the salt sodium phenoxide:

$$C_6H_5OH + NaOH \longrightarrow C_6H_5O^-Na^+ + H_2O$$

The corresponding reaction between NaOH and alcohols does not occur to a significant extent, although sodium ethoxide can be prepared by reaction of metallic sodium with anhydrous ethanol:

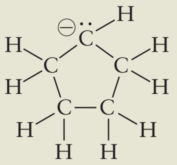
$$Na + C_2H_5OH \longrightarrow C_2H_5O^-Na^+ + \frac{1}{2}H_2$$

EXAMPLE 15.18

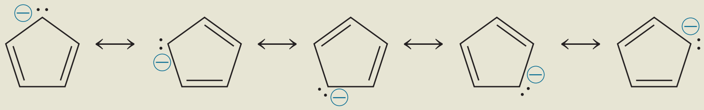
By using resonance Lewis structures, predict which will be the stronger acid: cyclopentane (C_5H_{10}) or cyclopentadiene (C_5H_6).

SOLUTION

We can write only one Lewis structure for the conjugate base of cyclopentane:



It is a very weak acid. In contrast, we can write five resonance structures for the conjugate base of cyclopentadiene:



This is very stable, so cyclopentadiene will be a stronger acid (its pK_a is 16).

Related Problems: 77, 78

CHAPTER SUMMARY

Acid-base reactions in aqueous solutions are of central importance in a wide variety of systems that include industrial manufacturing processes, ordinary household substances, and the life-sustaining reactions in living systems. The common feature shared by all acids and bases is that they modify the properties of the water in which they are dissolved. An acid increases the concentration of the hydronium ion H_3O^+ above its value in pure water, which is controlled by the ion product constant of water. A base increases the concentration of the hydroxide ion OH^- above the value it takes in pure water, due to the ion product constant of water. The concentration of the hydronium ion is conveniently expressed by pH, and that of the hydroxide by pOH. These quantities are related as $\text{pH} + \text{pOH} = 14$ by the ion product constant of water. Some acids and bases dissociate completely in solution to produce concentrations of hydronium and hydroxide equivalent to the concentration of parent acid or base with which the solutions were prepared. These are called strong acids and bases, and reactions of their solutions are completely described by the laws of stoichiometry. Most acids and bases dissociate only partially, so we must use the principles of chemical equilibrium to describe the concentration of hydronium and hydroxide in their solutions. These are the weak acids and bases, and description of their reactions requires methods of stoichiometry combined with methods of equilibrium. Acid-base neutralization reactions produce water and salts as their products. These reactions can be followed quantitatively and precisely by titration, as a means to determine the amount of acid or base in an unknown sample. When the salt of a weak acid is dissolved in water, hydrolysis of the anion produces the undissociated acid, and the solution is basic. Similarly, hydrolysis of the salt of a weak base produces an acidic solution. In both cases the pH is calculated by equilibrium methods. An especially interesting situation arises when a weak acid is dissolved along with one of its salts. The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The effect of acid rain on a stand of trees in the Great Smoky Mountains of the United States.

combination of weak acid equilibrium and hydrolysis—called a buffer solution—keeps the pH of the solution constant as small amounts of acid are added. This stabilization mechanism is extremely important in biochemical and biological situations, where success of various reactions depends critically on keeping pH constant. The extent of all these acid-base reactions can be correlated with the structures of their molecules. The extent of reaction is governed by the equilibrium constant, which in turn depends on the Gibbs standard free energy of formation of the reactants and products, which depends on their molecular structure.

CUMULATIVE EXERCISE

Acid Precipitation

Acid precipitation is a major environmental problem throughout the industrialized world. One major source is the burning of fossil fuels containing sulfur (coal, oil, and natural gas). The sulfur dioxide released into the air dissolves in water or, more seriously, may be oxidized further to sulfur trioxide. The SO_3 dissolves in water to form sulfuric acid:

$$SO_3(g) + H_2O(\ell) \longrightarrow H_2SO_4(aq)$$

The net effect is to increase the acidity of the rain, which damages trees, kills fish in lakes, dissolves stone, and corrodes metal.

(a) A sample of rainwater is tested for acidity by using two indicators. Addition of methyl orange to half of the sample gives a yellow color, and addition of methyl red to the other half gives a red color. Estimate the pH of the sample.

(b) The pH in acid rain can range down to 3 or even lower in heavily polluted areas. Calculate the concentrations of H_3O^+ and OH^- in a raindrop at pH 3.30 at 25°C.

(c) When SO_2 dissolves in water to form sulfurous acid, $H_2SO_3(aq)$, that acid can donate a hydrogen ion to water. Write a balanced chemical equation for this reaction, and identify the stronger Brønsted–Lowry acid and base in the equation.

(d) Ignore the further ionization of HSO_3^-, and calculate the pH of a solution whose initial concentration of H_2SO_3 is 4.0×10^{-4} M. (*Hint:* Use the quadratic equation in this case.)

(e) Now suppose that all the dissolved SO_2 from part (d) has been oxidized further to SO_3, so that 4.0×10^{-4} mol of H_2SO_4 is dissolved per liter. Calculate the pH in this case. (*Hint:* Because the first ionization of H_2SO_4 is that of a strong acid, the concentration of H_3O^+ can be written as 4.0×10^{-4} plus the unknown amount of dissociation from $HSO_4^-(aq)$.)

(f) Lakes have a natural buffering capacity, especially in regions where limestone gives rise to dissolved calcium carbonate. Write an equation for the effect of a small amount of acid rain containing sulfuric acid if it falls into a lake containing carbonate (CO_3^{2-}) ions. Discuss how the lake will resist further pH changes. What happens if a large excess of acid rain is deposited?

(g) A sample of 1.00 L of rainwater known to contain only sulfurous (and not sulfuric) acid is titrated with 0.0100 M NaOH. The equivalence point of the H_2SO_3/HSO_3^- titration is reached after 31.6 mL has been added. Calculate the original concentration of sulfurous acid in the sample, again ignoring any effect of SO_3^{2-} on the equilibria.

(h) Calculate the pH at the half-equivalence point, after 15.8 mL has been added. (*Hint:* Use the quadratic equation.)

Answers

(a) 4.4 to 4.8

(b) $[H_3O^+] = 5.0 \times 10^{-4}$ M; $[OH^-] = 2.0 \times 10^{-11}$ M

(c) $H_2SO_3(aq) + H_2O(\ell) \rightleftharpoons HSO_3^-(aq) + H_3O^+(aq)$. The stronger acid is H_3O^+, and the stronger base is HSO_3^-.

(d) The pH is 3.41.

(e) The pH is 3.11.

(f) The H_3O^+ in the sulfuric acid solution reacts according to $H_3O^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + H_2O(\ell)$. The HSO_4^- in the sulfuric acid reacts according to $HSO_4^-(aq) + CO_3^{2-}(aq) \rightleftharpoons SO_4^{2-}(aq) + HCO_3^-(aq)$. This gives rise to a HCO_3^-/CO_3^{2-} buffer that can resist further changes in pH. An excess of acid rain overwhelms the buffer and leads to the formation of H_2CO_3.

(g) 3.16×10^{-4} M

(h) The pH is 3.81.

CHAPTER REVIEW

Classification of Acids and Bases

- Brønsted-Lowry concept
    - Acids are proton donors.
    - Bases are proton acceptors.
    - Acid–base reactions are proton transfer reactions.
- Lewis concept
    - Acids are electron pair acceptors.
    - Bases are electron pair donors.
    - Acid–base reactions are electron pair transfer reactions.

The Brønsted–Lowry Description of Acids and Bases in Aqueous Solutions

- Autoionization of water
    - $K_w = [H_3O^+][OH^-] = 10^{-14}$ for pure water at 25°C
    - $[H_3O^+] = [OH^-] = 10^{-7}$ M
- Strong acids and bases
    - Strong acids and bases dissociate essentially completely in solution.
- The pH function
    - $pH = -\log [H_3O^+]$
    - $pH < 7$ acidic solution
    - $pH > 7$ basic solution
    - $pH = 7$ neutral solution

Acid and Base Strength

- For the reaction $HA(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + A^-(aq)$
    - $K_a = ([H_3O^+][A^-])/[HA]$
    - Strong acids have $K_a \gg 1$
- For the reaction $B(aq) + H_2O(\ell) \rightleftharpoons BH^+(aq) + OH^-(aq)$
    - $K_b = ([BH^+][OH^-])/[B]$
    - Strong bases have $K_b \gg 1$
- For a conjugate acid–base pair $K_a K_b = K_w$
- Stronger conjugate acids have weaker conjugate bases and *vice versa*.
- Strength of oxoacids: X—O—H increases as electronegativity of X increases
    - As X withdraws electron density from O, breaking the O—H bond to release H^+ becomes easier.
- Indicators respond to changes in pH because HIn and In^- have different colors. $K_a = ([H_3O^+][In^-])/[HIn]$

Equilibria Involving Weak Acids and Bases

- To describe weak acids
  let $x = [H_3O^+] = [A^-]$
  then $x^2/[HA] - x = K_a$
  If K_a is very small and initial concentration of HA ≥ 0.05 M, use the approximation $x^2/[HA] = K_a$.
  Otherwise, use the quadratic equation.
- Describe weak bases by the same procedure used for weak acids.
- Hydrolysis is the reaction of a salt of a weak base or a weak acid with water.
  The cation of a weak base acts as an acid to form the conjugate base and produce an acidic solution.
  The anion of a weak acid acts as a base to form the conjugate acid and produce a basic solution.
  For all conjugate acid–base pairs $K_b = K_w/K_a$.

Buffer Solutions

- A solution that contains a weak acid and its salt, or a weak base and its salt, in appreciable amounts resists changes in pH when either acid or base is added.
- The pH in a buffer solution is described by these approximate equations
  $[H_3O^+] \approx K_a[HA]_0/[A^-]_0$
  $pH \approx pK_a - \log_{10} [HA]_0/[A^-]_0$
- To describe the response of a buffer to added acid or base, follow the procedures demonstrated in Example 15.8

Acid–Base Titration Curves

- Titration curves for strong acids by strong bases and vice versa have four regions that can be calculated by using procedures of stoichiometry and definitions of solution concentration.
  1. Before any titrant is added. The concentration of the starting acid or base determines the pH.
  2. Before the equivalence point. Calculate the number of moles of acid or base remaining and divide by the total volume to calculate the concentration and determine the pH.
  3. At the equivalence point. pH = 7.
  4. After the equivalence point. Calculate the number of moles of excess acid or base and divide by the total volume to calculate the concentration and determine the pH.

  (**Note:** The choice of indicator is not critical in strong acid–strong base titrations since the slope of the transition at the equivalence point is very steep.)
- Titration curves for weak acids by strong bases and vice versa also have four regions. But each of these requires consideration of equilibrium in the solution and corresponds to a standard type of calculation illustrated in the chapter.
  1. Before any titrant is added. This is simply the ionization of a weak acid or based, as described in Examples 15.3 and 15.4.
  2. Before the equivalence point. This is a buffer solution, as described in Example 15.7.
  3. At the equivalence point. This is a hydrolysis problem. All of the initial acid or base has been converted to a salt, which hydrolyzes back to the acid or base, so the pH $\neq$ 7. See Example 15.6.
  4. After the equivalence point. The problem is very close to the titration of a strong acid or base. Calculate the number of moles of excess acid or base added and divide by the total volume to obtain the concentration and the pH.

  (**Note:** The choice of indicator is critical in weak acid–strong base and weak base–strong acid titrations because the slope of the transition is not so steep and the pH of the equivalence point can be very different from 7. pK_a (indicator) $\approx$ pH at the equivalence point.)

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Define an acid and a base in the Brønsted–Lowry and Lewis systems and give several examples of their reaction with a solvent (Section 15.1, Problems 1–12).
2. Define the pH function and convert between pH and $[H_3O^+]$ (Section 15.2, Problems 13–16).
3. State the relationship between the ionization constant for an acid and that for its conjugate base (Section 15.3, Problems 21–22).
4. Explain how indicators allow the pH of a solution to be estimated (Section 15.3, Problems 25–26).
5. Formulate the equilibrium expression for the ionization of a weak acid or base, and use it to determine the pH and fraction ionized (Section 15.4, Problems 27–36).
6. Explain the behavior of a buffer solution. Calculate its pH from the concentrations of its conjugate acid–base pair (Section 15.5, Problems 43–46).
7. Design a buffer system that will regulate the pH to a particular value (Section 15.5, Problems 47–50).
8. Calculate the pH at any stage in the titration of a strong acid or base by a strong base or acid (Section 15.6, Problems 51–52).
9. Calculate the pH at any stage in the titration of a weak acid or base by a strong base or acid (Section 15.6, Problems 53–62).
10. Calculate the concentrations of all the species present in a solution of a weak polyprotic acid (Section 15.7, Problems 63–68).
11. Outline the procedure for the exact treatment of acid–base equilibrium and use it to find the pH of a very dilute solution of a weak acid or base (Section 15.8, Problems 69–70).
12. Calculate the pH at selected points in the titration of a polyprotic acid (Section 15.8, Problems 71–72).
13. Use structure-function relations to predict effects of substitutions on relative acidities of organic acids (Section 15.9, Problems 73–80).

KEY EQUATIONS

$[H_3O^+][OH^-] = K_w$ **(Section 15.2)**

$\mathrm{pH} = -\log_{10}[H_3O^+]$ **(Section 15.2)**

$\mathrm{pH} < 7$ Acidic solution **(Section 15.2)**

$\mathrm{pH} = 7$ Neutral solution **(Section 15.2)**

$\mathrm{pH} > 7$ Basic solution **(Section 15.2)**

$$\frac{[H_3O^+][A^-]}{[HA]} = K_a$$ **(Section 15.3)**

$K_w = K_a K_b$ **(Section 15.3)**

$$\frac{[H_3O^+]}{K_a} = \frac{[HIn]}{[In^-]}$$ **(Section 15.3)**

$$\mathrm{pH} \approx \mathrm{p}K_a - \log_{10}\frac{[HA]_0}{[A^-]_0}$$ **(Section 15.5)**

$\Delta G° - \Delta G°' = -RT(\ln K_a - \ln K'_a) = 2.3\,RT(\mathrm{p}K_a - \mathrm{p}K'_a)$ **(Section 15.9)**

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

Classifications of Acids and Bases

1. Which of the following can act as Brønsted–Lowry acids? Give the formula of the conjugate Brønsted–Lowry base for each of them.
(a) Cl^- (b) HSO_4^- (c) NH_4^+
(d) NH_3 (e) H_2O

2. Which of the following can act as Brønsted–Lowry bases? Give the formula of the conjugate Brønsted–Lowry acid for each of them.
(a) F^- (b) SO_4^{2-} (c) O^{2-}
(d) OH^- (e) H_2O

3. Lemon juice contains citric acid ($C_6H_8O_7$). What species serves as a base when lemon juice is mixed with baking soda (sodium hydrogen carbonate) during the preparation of some lemon cookies?

4. A treatment recommended in case of accidental swallowing of ammonia-containing cleanser is to drink large amounts of diluted vinegar. Write an equation for the chemical reaction on which this procedure depends.

5. An important step in many industrial processes is the slaking of lime, in which water is added to calcium oxide to make calcium hydroxide.
(a) Write the balanced equation for this process.
(b) Can this be considered a Lewis acid–base reaction? If so, what is the Lewis acid and what is the Lewis base?

6. Silica (SiO_2) is an impurity that must be removed from a metal oxide or sulfide ore when the ore is being reduced to elemental metal. To do this, lime (CaO) is added. It reacts with the silica to form a slag of calcium silicate ($CaSiO_3$), which can be separated and removed from the ore.
(a) Write the balanced equation for this process.
(b) Can this be considered a Lewis acid–base reaction? If so, what is the Lewis acid and what is the Lewis base?

7. Chemists working with fluorine and its compounds sometimes find it helpful to think in terms of acid–base reactions in which the fluoride ion (F^-) is donated and accepted.
(a) Would the acid in this system be the fluoride donor or fluoride acceptor?
(b) Identify the acid and base in each of these reactions:

$$ClF_3O_2 + BF_3 \longrightarrow ClF_2O_2{\cdot}BF_4$$

$$TiF_4 + 2\,KF \longrightarrow K_2[TiF_6]$$

8. Researchers working with glasses often think of acid–base reactions in terms of oxide donors and oxide acceptors. The oxide ion is O^{2-}.
(a) In this system, is the base the oxide donor or the oxide acceptor?
(b) Identify the acid and base in each of these reactions:

$$2\,CaO + SiO_2 \longrightarrow Ca_2SiO_4$$

$$Ca_2SiO_4 + SiO_2 \longrightarrow 2\,CaSiO_3$$

$$Ca_2SiO_4 + CaO \longrightarrow Ca_3SiO_5$$

9. Identify each of the following oxides as an acid or base anhydride. Write the chemical formula and give the name of the acid or base formed upon reaction with water.
(a) MgO (b) Cl_2O
(c) SO_3 (d) Cs_2O

10. Write the chemical formula and give the name of the anhydride corresponding to each of the following acids or bases, and identify it as an acid or base anhydride.
(a) H_3AsO_4 (b) H_2MoO_4
(c) RbOH (d) H_2SO_3

11. Tin(II) oxide is amphoteric. Write balanced chemical equations for its reactions with an aqueous solution of hydrochloric acid and with an aqueous solution of sodium hydroxide. (**Note:** The hydroxide complex ion of tin(II) is $[Sn(OH)_3]^-$.)

12. Zinc oxide is amphoteric. Write balanced chemical equations for its reactions with an aqueous solution of hydrochloric acid and with an aqueous solution of sodium hydroxide. (**Note:** The hydroxide complex ion of zinc is $[Zn(OH)_4]^{2-}$.)

Properties of Acids and Bases in Aqueous Solutions: The Brønsted–Lowry Scheme

13. The concentration of H_3O^+ in a sample of wine is 2.0×10^{-4} M. Calculate the pH of the wine.

14. The concentration of OH^- in a solution of household bleach is 3.6×10^{-2} M. Calculate the pH of the bleach.

15. The pH of normal human urine is in the range of 5.5 to 6.5. Compute the range of the H_3O^+ concentration and the range of the OH^- concentration in normal urine.

16. The pH of normal human blood is in the range of 7.35 to 7.45. Compute the range of the concentration of H_3O^+ and the range of the OH^- concentration in normal blood.

17. The pK_w of seawater at 25°C is 13.776. This differs from the usual pK_w of 14.00 at this temperature because dissolved salts make seawater a nonideal solution. If the pH in seawater is 8.00, what are the concentrations of H_3O^+ and OH^- in seawater at 25°C?

18. At body temperature (98.6°F = 37.0°C), K_w has the value 2.4×10^{-14}. If the pH of blood is 7.4 under these conditions, what are the concentrations of H_3O^+ and OH^-?

19. When placed in water, potassium starts to react instantly and continues to react with great vigor. On the basis of this information, select the better of the following two equations to represent the reaction.

$$2\,K(s) + 2\,H_2O(\ell) \longrightarrow 2\,KOH(aq) + H_2(g)$$

$$2\,K(s) + 2\,H_3O^+(aq) \longrightarrow 2\,K^+(aq) + H_2(g) + 2H_2O(\ell)$$

State the reason for your choice.

20. Molecules of *t*-butyl chloride, $(CH_3)_3CCl$, react very slowly when mixed with water at low pH to give *t*-butyl alcohol, $(CH_3)_3COH$. When the pH is raised, the reaction takes place rapidly. Write an equation or equations to explain these facts.

Acid and Base Strength

21. Ephedrine ($C_{10}H_{15}ON$) is a base that is used in nasal sprays as a decongestant.
 (a) Write an equation for its equilibrium reaction with water.
 (b) The K_b for ephedrine is 1.4×10^{-4}. Calculate the K_a for its conjugate acid.
 (c) Is ephedrine a weaker or a stronger base than ammonia?

22. Niacin (C_5H_4NCOOH), one of the B vitamins, is an acid.
 (a) Write an equation for its equilibrium reaction with water.
 (b) The K_a for niacin is 1.5×10^{-5}. Calculate the K_b for its conjugate base.
 (c) Is the conjugate base of niacin a stronger or a weaker base than pyridine, C_5H_5N?

23. Use the data in Table 15.2 to determine the equilibrium constant for the reaction.

$$HClO_2(aq) + NO_2^-(aq) \rightleftharpoons HNO_2(aq) + ClO_2^-(aq)$$

Identify the stronger Brønsted–Lowry acid and the stronger Brønsted–Lowry base.

24. Use the data in Table 15.2 to determine the equilibrium constant for the reaction

$$HPO_4^{2-} + HCO_3^- \rightleftharpoons PO_4^{3-} + H_2CO_3$$

Identify the stronger Brønsted–Lowry acid and the stronger Brønsted–Lowry base.

25. (a) Which is the stronger acid—the acidic form of the indicator bromocresol green or the acidic form of methyl orange?
 (b) A solution is prepared in which bromocresol green is green and methyl orange is orange. Estimate the pH of this solution.

26. (a) Which is the stronger base—the basic form of the indicator cresol red or the basic form of thymolphthalein?
 (b) A solution is prepared in which cresol red is red and thymolphthalein is colorless. Estimate the pH of this solution.

Equilibria Involving Weak Acids and Bases

27. Aspirin is acetylsalicylic acid, $HC_9H_7O_4$, which has a K_a of 3.0×10^{-4}. Calculate the pH of a solution made by dissolving 0.65 g of acetylsalicylic acid in water and diluting to 50.0 mL.

28. Vitamin C is ascorbic acid ($HC_6H_7O_6$), for which K_a is 8.0×10^{-5}. Calculate the pH of a solution made by dissolving a 500-mg tablet of pure vitamin C in water and diluting to 100 mL.

29. (a) Calculate the pH of a 0.20 M solution of benzoic acid at 25°C.
 (b) How many moles of acetic acid must be dissolved per liter of water to obtain the same pH as that from part (a)?

30. (a) Calculate the pH of a 0.35 M solution of propionic acid at 25°C.
 (b) How many moles of formic acid must be dissolved per liter of water to obtain the same pH as that from part (a)?

31. Iodic acid (HIO_3) is fairly strong for a weak acid, having a K_a equal to 0.16 at 25°C. Compute the pH of a 0.100 M solution of HIO_3.

32. At 25°C, the K_a of pentafluorobenzoic acid (C_6F_5COOH) is 0.033. Suppose 0.100 mol of pentafluorobenzoic acid is dissolved in 1.00 L of water. What is the pH of this solution?

33. Papaverine hydrochloride ($papH^+Cl^-$) is a drug used as a muscle relaxant. It is a weak acid. At 25°C, a 0.205 M solution of $papH^+Cl^-$ has a pH of 3.31. Compute the K_a of the $papH^+$ ion.

34. The unstable weak acid 2-germaacetic acid (GeH_3COOH) is derived structurally from acetic acid (CH_3COOH) by having a germanium atom replace one of the carbon atoms. At 25°C, a 0.050 M solution of 2-germaacetic acid has a pH of 2.42. Compute the K_1 of 2-germaacetic acid and compare it with that of acetic acid.

35. Morphine is a weak base for which K_b is 8×10^{-7}. Calculate the pH of a solution made by dissolving 0.0400 mol of morphine in water and diluting to 600.0 mL.

36. Methylamine is a weak base for which K_b is 4.4×10^{-4}. Calculate the pH of a solution made by dissolving 0.070 mol of methylamine in water and diluting to 800.0 mL.

37. The pH at 25°C of an aqueous solution of hydrofluoric acid, HF, is 2.13. Calculate the concentration of HF in this solution, in moles per liter.

38. The pH at 25°C of an aqueous solution of sodium cyanide (NaCN) is 11.50. Calculate the concentration of CN^- in this solution, in moles per liter.

39. You have 50.00 mL of a solution that is 0.100 M in acetic acid, and you neutralize it by adding 50.00 mL of a solution that is 0.100 M in sodium hydroxide. The pH of the resulting solution is not 7.00. Explain why. Is the pH of the solution greater than or less than 7?

40. A 75.00-mL portion of a solution that is 0.0460 M in $HClO_4$ is treated with 150.00 mL of 0.0230 M KOH(*aq*). Is the pH of the resulting mixture greater than, less than, or equal to 7.0? Explain.

41. Suppose a 0.100 M solution of each of the following substances is prepared. Rank the pH of the resulting solutions from lowest to highest: NH_4Br, NaOH, KI, $NaCH_3COO$, HCl.

42. Suppose a 0.100 M solution of each of the following substances is prepared. Rank the pH of the resulting solutions from lowest to highest: KF, NH_4I, HBr, NaCl, LiOH.

Buffer Solutions

43. "Tris" is short for tris(hydroxymethyl)aminomethane. This weak base is widely used in biochemical research for the preparation of buffers. It offers low toxicity and a pK_b (5.92 at 25°C) that is convenient for the control of pH in clinical applications. A buffer is prepared by mixing 0.050 mol of tris with 0.025 mol of HCl in a volume of 2.00 L. Compute the pH of the solution.

44. "Bis" is short for bis(hydroxymethyl)aminomethane. It is a weak base that is closely related to tris (see problem 43) and has similar properties and uses. Its pK_b is 8.8 at 25°C. A buffer is prepared by mixing 0.050 mol of bis with 0.025

mol of HCl in a volume of 2.00 L (the same proportions as in the preceding problem). Compute the pH of the solution.

45. **(a)** Calculate the pH in a solution prepared by dissolving 0.050 mol of acetic acid and 0.020 mol of sodium acetate in water and adjusting the volume to 500 mL.
(b) Suppose 0.010 mol of NaOH is added to the buffer from part (a). Calculate the pH of the solution that results.

46. Sulfanilic acid ($NH_2C_6H_4SO_3H$) is used in manufacturing dyes. It ionizes in water according to the equilibrium equation

$$NH_2C_6H_4SO_3H(aq) + H_2O(\ell) \rightleftharpoons NH_2C_6H_4SO_3^-(aq) + H_3O^+(aq) \quad K_a = 5.9 \times 10^{-4}$$

A buffer is prepared by dissolving 0.20 mol of sulfanilic acid and 0.13 mol of sodium sulfanilate ($NaNH_2C_6H_4SO_3$) in water and diluting to 1.00 L.
(a) Compute the pH of the solution.
(b) Suppose 0.040 mol of HCl is added to the buffer. Calculate the pH of the solution that results.

47. A physician wishes to prepare a buffer solution at pH = 3.82 that efficiently resists changes in pH yet contains only small concentrations of the buffering agents. Determine which one of the following weak acids, together with its sodium salt, would probably be best to use: *m*-chlorobenzoic acid, $K_a = 1.04 \times 10^{-4}$; *p*-chlorocinnamic acid, $K_a = 3.89 \times 10^{-5}$; 2,5-dihydroxybenzoic acid, $K_a = 1.08 \times 10^{-3}$; or acetoacetic acid, $K_a = 2.62 \times 10^{-4}$. Explain.

48. Suppose you were designing a buffer system for imitation blood and wanted the buffer to maintain the blood at the realistic pH of 7.40. All other things being equal, which buffer system would be preferable: H_2CO_3/HCO_3^- or $H_2PO_4^-/HPO_4^{2-}$? Explain.

49. You have at your disposal an ample quantity of a solution of 0.0500 M NaOH and 500 mL of a solution of 0.100 M formic acid (HCOOH). How much of the NaOH solution should be added to the acid solution to produce a buffer of pH 4.00?

50. You have at your disposal an ample quantity of a solution of 0.100 M HCl and 400 mL of a solution of 0.0800 M NaCN. How much of the HCl solution should be added to the NaCN solution to produce a buffer of pH 9.60?

Acid–Base Titration Curves

51. Suppose 100.0 mL of a 0.3750 M solution of the strong base $Ba(OH)_2$ is titrated with a 0.4540 M solution of the strong acid $HClO_4$. The neutralization reaction is

$$Ba(OH)_2(aq) + 2\ HClO_4(aq) \longrightarrow Ba(ClO_4)_2(aq) + 2\ H_2O(\ell)$$

Compute the pH of the titration solution before any acid is added, when the titration is 1.00 mL short of the equivalence point, when the titration is at the equivalence point, and when the titration is 1.00 mL past the equivalence point. (**Note:** Each mole of $Ba(OH)_2$ gives *two* moles of OH^- in solution.)

52. A sample containing 26.38 mL of 0.1439 M HBr is titrated with a solution of NaOH having a molarity of 0.1219 M. Compute the pH of the titration solution before any base is added, when the titration is 1.00 mL short of the equivalence point, when the titration is at the equivalence point, and when the titration is 1.00 mL past the equivalence point.

53. A sample containing 50.00 mL of 0.1000 M hydrazoic acid (HN_3) is being titrated with 0.1000 M sodium hydroxide. Compute the pH before any base is added, after the addition of 25.00 mL of the base, after the addition of 50.00 mL of the base, and after the addition of 51.00 mL of the base.

54. A sample of 50.00 mL of 0.1000 M aqueous solution of chloroacetic acid, $CH_2ClCOOH$ ($K_1 = 1.4 \times 10^{-3}$), is titrated with a 0.1000 M NaOH solution. Calculate the pH at the following stages in the titration, and plot the titration curve: 0, 5.00, 25.00, 49.00, 49.90, 50.00, 50.10, and 55.00 mL NaOH.

55. The base ionization constant of ethylamine ($C_2H_5NH_2$) in aqueous solution is $K_b = 6.41 \times 10^{-4}$ at 25°C. Calculate the pH for the titration of 40.00 mL of a 0.1000 M solution of ethylamine with 0.1000 M HCl at the following volumes of added HCl: 0, 5.00, 20.00, 39.90, 40.00, 40.10, and 50.00 mL.

56. Ammonia is a weak base with a K_b of 1.8×10^{-5}. A 140.0-mL sample of a 0.175 M solution of aqueous ammonia is titrated with a 0.106 M solution of the strong acid HCl. The reaction is

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

Compute the pH of the titration solution before any acid is added, when the titration is at the half-equivalence point, when the titration is at the equivalence point, and when the titration is 1.00 mL past the equivalence point.

57. Sodium benzoate, the sodium salt of benzoic acid, is used as a food preservative. A sample containing solid sodium benzoate mixed with sodium chloride is dissolved in 50.0 mL of 0.500 M HCl, giving an acidic solution (benzoic acid mixed with HCl). This mixture is then titrated with 0.393 M NaOH. After the addition of 46.50 mL of the NaOH solution, the pH is found to be 8.2. At this point, the addition of one more drop (0.02 mL) of NaOH raises the pH to 9.3. Calculate the mass of sodium benzoate (NaC_6H_5COO) in the original sample. (*Hint:* At the equivalence point, the *total* number of moles of acid [here HCl] equals the *total* number of moles of base [here, both NaOH and NaC_6H_5COO].)

58. An antacid tablet (such as Tums or Rolaids) weighs 1.3259 g. The only acid-neutralizing ingredient in this brand of antacid is $CaCO_3$. When placed in 12.07 mL of 1.070 M HCl, the tablet fizzes merrily as $CO_2(g)$ is given off. After all of the CO_2 has left the solution, an indicator is added, followed by 11.74 mL of 0.5310 M NaOH. The indicator shows that at this point the solution is definitely basic. Addition of 5.12 mL of 1.070 M HCl makes the solution acidic again. Then 3.17 mL of the 0.5310 M NaOH brings the titration exactly to an endpoint, as signaled by the indicator. Compute the percentage by mass of $CaCO_3$ in the tablet.

59. What is the mass of diethylamine, $(C_2H_5)_2NH$, in 100.0 mL of an aqueous solution if it requires 15.90 mL of 0.0750 M HCl to titrate it to the equivalence point? What is the pH at the equivalence point if $K_b = 3.09 \times 10^{-4}$? What would be a suitable indicator for the titration?

60. A chemist who works in the process laboratory of the Athabasca Alkali Company makes frequent analyses of ammonia recovered from the Solvay process for making sodium carbonate. What is the pH at the equivalence point if she titrates the aqueous ammonia solution (approximately 0.10 M) with a strong acid of comparable concentration? Select an indicator that would be suitable for the titration.

61. If 50.00 mL of a 0.200 M solution of the weak base *N*-ethylmorpholine ($C_6H_{13}NO$) is mixed with 8.00 mL of 1.00 M HCl and then diluted to a final volume of 100.0 mL with water, the result is a buffer with a pH of 7.0. Compute the K_b of *N*-ethylmorpholine.

62. The sodium salt of cacodylic acid, a weak acid, has the formula $NaO_2As(CH_3)_2{\cdot}3H_2O$. Its molar mass is 214.02 g mol^{-1}. A solution is prepared by mixing 21.40 g of this substance with enough water to make 1.000 L of solution. Then 50.00 mL of the sodium cacodylate solution is mixed with 29.55 mL of 0.100 M HCl and enough water to bring the volume to a total of 100.00 mL. The pH of the solution is 6.00. Determine the K_a of cacodylic acid.

Polyprotic Acids

63. Arsenic acid (H_3AsO_4) is a weak triprotic acid. Given the three acid ionization constants from Table 15.2 and an initial concentration of arsenic acid (before ionization) of 0.1000 M, calculate the equilibrium concentrations of H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}, and H_3O^+.

64. Phthalic acid ($H_2C_8H_4O_4$, abbreviated H_2Ph) is a diprotic acid. Its ionization in water at 25°C takes place in two steps:

$$H_2Ph(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HPh^-(aq) \qquad K_{a1} = 1.26 \times 10^{-3}$$

$$HPh^-(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + Ph^{2-}(aq) \qquad K_{a2} = 3.10 \times 10^{-6}$$

If 0.0100 mol of phthalic acid is dissolved per liter of water, calculate the equilibrium concentrations of H_2Ph, HPh^-, Ph^{2-}, and H_3O^+.

65. A solution as initially prepared contains 0.050 mol L^{-1} of phosphate ion (PO_4^{3-}) at 25°C. Given the three acid ionization constants from Table 15.2, calculate the equilibrium concentrations of PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4, and OH^-.

66. Oxalic acid ionizes in two stages in aqueous solution:

$$H_2C_2O_4(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HC_2O_4^-(aq) \qquad K_{a1} = 5.9 \times 10^{-2}$$

$$HC_2O_4^-(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + C_2O_4^{2-}(aq) \qquad K_{a2} = 6.4 \times 10^{-5}$$

Calculate the equilibrium concentrations of $C_2O_4^{2-}$, $HC_2O_4^-$, $H_2C_2O_4$, and OH^- in a 0.10 M solution of sodium oxalate ($Na_2C_2O_4$).

67. The pH of a normal raindrop is 5.60. Compute the concentrations of $H_2CO_3(aq)$, $HCO_3^-(aq)$, and $CO_3^{2-}(aq)$ in this raindrop if the total concentration of dissolved carbonates is 1.0×10^{-5} mol L^{-1}.

68. The pH of a drop of acid rain is 4.00. Compute the concentrations of $H_2CO_3(aq)$, $HCO_3^-(aq)$, and $CO_3^{2-}(aq)$ in the acid raindrop if the total concentration of dissolved carbonates is 3.6×10^{-5} mol L^{-1}.

A DEEPER LOOK . . . Exact Treatment of Acid–Base Equilibria

69. Thiamine hydrochloride (vitamin B_1 hydrochloride, $HC_{12}H_{17}ON_4SCl_2$) is a weak acid with $K_a = 3.4 \times 10^{-7}$. Suppose 3.0×10^{-5} g of thiamine hydrochloride is dissolved in 1.00 L of water. Calculate the pH of the resulting solution. (*Hint:* This is a sufficiently dilute solution that the autoionization of water cannot be neglected.)

70. A sample of vinegar contains 40.0 g of acetic acid (CH_3COOH) per liter of solution. Suppose 1.00 mL is removed and diluted to 1.00 L, and 1.00 mL of *that* solution is removed and diluted to 1.00 L. Calculate the pH of the resulting solution. (*Hint:* This is a sufficiently dilute solution that the autoionization of water cannot be neglected.)

71. At 25°C, 50.00 mL of a 0.1000 M solution of maleic acid, a diprotic acid whose ionization constants are $K_{a1} = 1.42 \times 10^{-2}$ and $K_{a2} = 8.57 \times 10^{-7}$, is titrated with a 0.1000 M NaOH solution. Calculate the pH at the following volumes of added base: 0, 5.00, 25.00, 50.00, 75.00, 99.90, 100.00, and 105.00 mL.

72. Quinine ($C_{20}H_{24}O_2N_2$) is a water-soluble base that ionizes in two stages, with $K_{b1} = 3.31 \times 10^{-6}$ and $K_{b2} = 1.35 \times 10^{-10}$, at 25°C. Calculate the pH during the titration of an aqueous solution of 1.622 g of quinine in 100.00 mL of water as a function of the volume of added 0.1000 M HCl solution at the following volumes: 0, 25.00, 50.00, 75.00, 99.90, 100.00, and 105.00 mL.

Organic Acids and Bases: Structure and Reactivity

73. Use data from Table 15.4 to estimate the stabilization (in kJ per mol) associated with substituting a phenyl ($-C_6H_5$) group for one of the hydrogen atoms in methane. Assume that the effect on the pK_a enters entirely through the greater energetic stability of the conjugate base.

74. Use data from Table 15.4 to estimate the stabilization (in kJ per mol) associated with substituting a nitro ($-NO_2$) group for one of the hydrogen atoms in methane. Assume that the effect on the pK_a enters entirely through the greater energetic stability of the conjugate base.

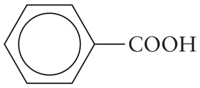
75. Propionic acid, CH_3CH_2COOH, has a pK_a of 4.9. Compare this with the diprotic succinic acid, $HOOCCH_2CH_2COOH$. Will the pK_{a1} and pK_{a2} of succinic acid be larger than or smaller than 4.9?

76. Predict the relative magnitudes of the pK_a's for a carboxylic acid, RCOOH, a ketone, $RCOCH_3$, and an amide, $RCONH_2$.

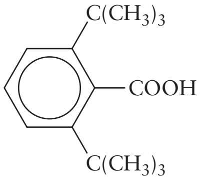
77. Which will be the stronger acid: benzene (C_6H_6) or cyclohexane (C_6H_{12})? Explain by using resonance Lewis structures.

78. Which will be the stronger acid: propene ($CH_2{=}CHCH_3$) or propane (C_3H_8)? Explain by using resonance Lewis structures.

79. For each of the following pairs of molecules, predict which is the stronger acid.
(a) CF_3COOH or CCl_3COOH.
(b) $CH_2FCH_2CH_2COOH$ or $CH_3CH_2CHFCOOH$
(c)

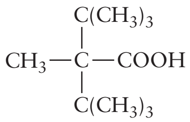


or



80. For each of the following pairs of molecules, predict which is the stronger acid.
(a)

CH_3CH_2COOH or



$$CH_3-\underset{\displaystyle C(CH_3)_3}{\overset{\displaystyle C(CH_3)_3}{\overset{|}{\underset{|}{C}}}}-COOH$$

(b) CI_3COOH or CCl_3COOH
(c) $CH_3CHClCH_2COOH$ or $CH_3CH_2CHClCOOH$

ADDITIONAL PROBLEMS

81. Although acetic acid is normally regarded as a weak acid, it is about 34% dissociated in a 10^{-4} M solution at 25°C. It is less than 1% dissociated in 1 M solution. Discuss this variation in degree of dissociation with dilution in terms of Le Châtelier's principle, and explain how it is consistent with the supposed constancy of equilibrium constants.

82. Suppose that a 0.10 M aqueous solution of a monoprotic acid HX has just 11 times the conductivity of a 0.0010 M aqueous solution of HX. What is the approximate dissociation constant of HX? (*Hint:* In thinking about this problem, consider what the ratio of the conductivities would be if HX were a strong acid and if HX were extremely weak, as limiting cases.)

83. The ionization constant of chloroacetic acid ($ClCH_2COOH$) in water is 1.528×10^{-3} at 0°C and 1.230×10^{-3} at 40°C. Calculate the enthalpy of ionization of the acid in water, assuming that ΔH and ΔS are constant over this range of temperature.

84. The autoionization constant of water (K_w) is 1.139×10^{-15} at 0°C and 9.614×10^{-14} at 60°C.
(a) Calculate the enthalpy of autoionization of water.

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

(b) Calculate the entropy of autoionization of water.
(c) At what temperature will the pH of pure water be 7.00, from these data?

85. Calculate the concentrations of H_3O^+ and OH^- at 25°C in the following:
(a) Orange juice (pH 2.8)
(b) Tomato juice (pH 3.9)
(c) Milk (pH 4.1)
(d) Borax solution (pH 8.5)
(e) Household ammonia (pH 11.9)

86. Try to choose which of the following is the pH of a 6.44×10^{-10} M $Ca(OH)_2(aq)$ solution, without doing any written calculations.
(a) 4.81
(b) 5.11
(c) 7.00
(d) 8.89
(e) 9.19

87. $Cl_2(aq)$ reacts with $H_2O(\ell)$ as follows:

$$Cl_2(aq) + 2\,H_2O(\ell) \rightleftharpoons H_3O^+(aq) + Cl^-(aq) + HOCl(aq)$$

For an experiment to succeed, $Cl_2(aq)$ must be present, but the amount of $Cl^-(aq)$ in the solution must be minimized. For this purpose, should the pH of the solution be high, low, or neutral? Explain.

88. Use the data in Table 15.2 to determine the equilibrium constant for the reaction

$$H_2PO_4^-(aq) + 2\,CO_3^{2-}(aq) \rightleftharpoons PO_4^{3-}(aq) + 2\,HCO_3^-(aq)$$

89. The first acid ionization constant of the oxoacid H_3PO_2 is 8×10^{-2}. What molecular structure do you predict for H_3PO_2? Will this acid be monoprotic, diprotic, or triprotic in aqueous solution?

90. Oxoacids can be formed that involve several central atoms of the same chemical element. An example is $H_3P_3O_9$, which can be written $P_3O_6(OH)_3$. (Sodium salts of these polyphosphoric acids are used as "builders" in detergents to improve their cleaning power.) In such a case, we would expect acid strength to correlate approximately with the *ratio* of the number of lone oxygen atoms to the number of central atoms (this ratio is 6:3 for $H_3P_3O_9$, for example). Rank the following in order of increasing acid strength: H_3PO_4, $H_3P_3O_9$, $H_4P_2O_6$, $H_4P_2O_7$, $H_5P_3O_{10}$. Assume that no hydrogen atoms are directly bonded to phosphorus in these compounds.

91. Urea (NH_2CONH_2) is a component of urine. It is a very weak base, having an estimated pK_b of 13.8 at room temperature.
(a) Write the formula of the conjugate acid of urea.
(b) Compute the equilibrium concentration of urea in a solution that contains no urea but starts out containing 0.15 mol L^{-1} of the conjugate acid of urea.

92. Exactly 1.0 L of solution of acetic acid gives the same color with methyl red as 1.0 L of a solution of hydrochloric acid. Which solution will neutralize the greater amount of 0.10 M $NaOH(aq)$? Explain.

* **93.** The K_a for acetic acid drops from 1.76×10^{-5} at 25°C to 1.63×10^{-5} at 50°C. Between the same two temperatures, K_w increases from 1.00×10^{-14} to 5.47×10^{-14}. At 50°C the density of a 0.10 M solution of acetic acid is 98.81% of its density at 25°C. Will the pH of a 0.10 M solution of acetic acid in water increase, decrease, or remain the same when it is heated from 25°C to 50°C? Explain.

94. Calculate the pH of a solution that is prepared by dissolving 0.23 mol of hydrofluoric acid (HF) and 0.57 mol of hypochlorous acid (HClO) in water and diluting to 3.60 L. Also, calculate the equilibrium concentrations of HF, F^-, HClO, and ClO^-. (*Hint:* The pH will be determined by the stronger acid of this pair.)

95. For each of the following compounds, indicate whether a 0.100 M aqueous solution is acidic ($pH < 7$), basic ($pH > 7$), or neutral ($pH = 7$): HCl, NH_4Cl, KNO_3, Na_3PO_4, $NaCH_3COO$.

***96.** Calculate $[H_3O^+]$ in a solution that contains 0.100 mol of NH_4CN per liter.

$$NH_4^+(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + NH_3(aq) \qquad K_a = 5.6 \times 10^{-10}$$

$$HCN(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + CN^-(aq) \qquad K_a = 6.17 \times 10^{-10}$$

97. Discuss the justification for this statement: "Although one does not normally regard NH_4^+ as an acid, it is actually only slightly weaker as an acid than hydrocyanic acid, HCN, in aqueous solution."

***98.** Imagine that you want to do physiological experiments at a pH of 6.0 and the organism with which you are working is sensitive to most available materials other than a certain weak acid, H_2Z, and its sodium salts. K_{a1} and K_{a2} for H_2Z are 3×10^{-1} M and 5×10^{-7} M. You have available 1.0 M aqueous H_2Z and 1.0 M NaOH. How much of the NaOH solution should be added to 1.0 L of the acid solution to give a buffer at pH = 6.0?

99. A buffer solution is prepared by mixing 1.00 L of 0.050 M pentafluorobenzoic acid (C_6F_5COOH) and 1.00 L of 0.060 M sodium pentafluorobenzoate (NaC_6F_5COO). The K_a of this weak acid is 0.033. Determine the pH of the buffer solution.

100. A chemist needs to prepare a buffer solution with pH = 10.00 and has both Na_2CO_3 and $NaHCO_3$ in pure crystalline form. What mass of each should be dissolved in 1.00 L of solution if the combined mass of the two salts is to be 10.0 g?

101. Which of these procedures would *not* make a pH = 4.75 buffer?

(a) Mix 50.0 mL of 0.10 M acetic acid and 50.0 mL of 0.10 M sodium acetate.

(b) Mix 50.0 mL of 0.20 M acetic acid and 50.0 mL of 0.10 M NaOH.

(c) Start with 50.0 mL of 0.20 M acetic acid and add a solution of strong base until the pH equals 4.75.

(d) Start with 50.0 mL of 0.20 M HCl and add a solution of strong base until the pH equals 4.75.

(e) Start with 100.0 mL of 0.20 M sodium acetate and add 50.0 mL of 0.20 M HCl.

102. It takes 4.71 mL of 0.0410 M NaOH to titrate a 50.00-mL sample of flat (no CO_2) GG's Cola to a pH of 4.9. At this point the addition of one more drop (0.02 mL) of NaOH raises the pH to 6.1. The only acid in GG's Cola is phosphoric acid. Compute the concentration of phosphoric acid in this cola. Assume that the 4.71 mL of base removes only the first hydrogen from the H_3PO_4; that is, assume that the reaction is

$$H_3PO_4(aq) + OH^-(aq) \longrightarrow H_2O(\ell) + H_2PO_4^-(aq)$$

***103.** Sodium carbonate exists in various crystalline forms with different amounts of water of crystallization, including Na_2CO_3, $Na_2CO_3{\cdot}10H_2O$, and others. The water of crystallization can be driven off by heating; the amount of water removed depends on the temperature and duration of heating.

A sample of $Na_2CO_3{\cdot}10H_2O$ had been heated inadvertently, and it was not known how much water had been removed. A 0.200-g sample of the solid that remained after the heating was dissolved in water, 30.0 mL of 0.100 M NaOH was added, and the CO_2 formed was removed. The solution was acidic; 6.4 mL of 0.200 M NaOH was needed to neutralize the excess acid. What fraction of the water had been driven from the $Na_2CO_3{\cdot}10H_2O$?

104. An aqueous solution of sodium carbonate, Na_2CO_3, is titrated with strong acid to a point at which two H^+ ions have reacted with each carbonate ion. (a) If 20.0 mL of the carbonate solution reacts with just 40.0 mL of 0.50 M acid, what is the molarity of the carbonate solution? (b) If the solution contains 5.0 percent by mass sodium carbonate, what is the density of the solution? (c) Suppose that you wanted to prepare a liter of an identical solution by starting with crystalline sodium carbonate decahydrate, $Na_2CO_3{\cdot}10H_2O$, rather than with solid Na_2CO_3 itself. How much of this substance would you need?

105. Three flasks, labeled *A, B,* and *C,* contained aqueous solutions of the same pH. It was known that one of the solutions was 1.0×10^{-3} M in nitric acid, one was 6×10^{-3} M in formic acid, and one was 4×10^{-2} M in the salt formed by the weak organic base aniline with hydrochloric acid ($C_6H_5NH_3Cl$). (Formic acid is monoprotic.) (a) Describe a procedure for identifying the solutions. (b) Compare qualitatively (on the basis of the preceding information) the strengths of nitric and formic acids with each other and with the acid strength of the anilinium ion, $C_6H_5NH_3^+$. (c) Show how the information given may be used to derive values for K_a for formic acid and K_b for aniline. Derive these values.

106. Novocain, the commonly used local anaesthetic, is a weak base with $K_b = 7 \times 10^{-6}$ M. (a) If you had a 0.0200 M solution of Novocain in water, what would be the approximate concentration of OH^- and the pH? (b) Suppose that you wanted to determine the concentration of Novocain in a solution that is about 0.020 M by titration with 0.020 M HCl. Calculate the expected pH at the equivalence point.

107. A 0.1000 M solution of a weak acid, HA, requires 50.00 mL of 0.1000 M NaOH to titrate it to its equivalence point. The pH of the solution is 4.50 when only 40.00 mL of the base has been added.

(a) Calculate the ionization constant K_a of the acid.

(b) Calculate the pH of the solution at the equivalence point.

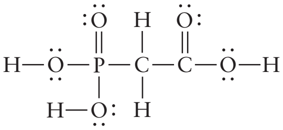
108. The chief chemist of Victory Vinegar Works, Ltd., interviews two chemists for employment. He states, "Quality control requires that our high-grade vinegar contain 5.00 ± 0.01% acetic acid by mass. How would you analyze our product to ensure that it meets this specification?"

Anne Dalton says, "I would titrate a 50.00-mL sample of the vinegar with 1.000 M NaOH, using phenolphthalein to detect the equivalence point to within ±0.02 mL of base."

Charlie Cannizzaro says, "I would use a pH meter to determine the pH to ±0.01 pH units and interface it with a computer to print out the mass percentage of acetic acid."

Which candidate did the chief chemist hire? Why?

109. Phosphonocarboxylic acid



effectively inhibits the replication of the herpes virus. Structurally, it is a combination of phosphoric acid and acetic acid. It can donate three protons. The equilibrium constant values are $K_{a1} = 1.0 \times 10^{-2}$, $K_{a2} = 7.8 \times 10^{-6}$, and $K_{a3} = 2.0 \times 10^{-9}$. Enough phosphonocarboxylic acid is added to blood (pH 7.40) to make its total concentration 1.0×10^{-5} M. The pH of the blood does not change. Determine the concentrations of all four forms of the acid in this mixture.

110. Egg whites contain dissolved carbon dioxide and water, which react together to give carbonic acid (H_2CO_3). In the few days after an egg is laid, it loses carbon dioxide through its shell. Does the pH of the egg white increase or decrease during this period?

111. If you breathe too rapidly (hyperventilate), the concentration of dissolved CO_2 in your blood drops. What effect does this have on the pH of the blood?

112. A reference book states that a saturated aqueous solution of potassium hydrogen tartrate is a buffer with a pH of 3.56. Write two chemical equations that show the buffer action of this solution. (Tartaric acid is a diprotic acid with the formula $H_2C_4H_4O_6$. Potassium hydrogen tartrate is $KHC_4H_4O_6$.)

***113.** Glycine, the simplest amino acid, has both an acid group and a basic group in its structure ($H_2N{-}CH_2{-}COOH$). In aqueous solution it exists predominantly as a self-neutralized species called a zwitterion ($H_3\overset{+}{N}{-}CH_2{-}COO^-$). The zwitterion therefore behaves both as an acid and as a base, according to the equilibria at 25°C:

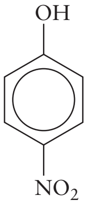
$$H_3\overset{+}{N}{-}CH_2{-}COO^-(aq) + H_2O(\ell) \rightleftharpoons H_2N{-}CH_2{-}COO^-(aq) + H_3O^+(aq) \qquad K_a = 1.7 \times 10^{-10}$$

$$H_3\overset{+}{N}{-}CH_2{-}COO^-(aq) + H_2O(\ell) \rightleftharpoons H_3\overset{+}{N}{-}CH_2{-}COOH(aq) + OH^-(aq) \qquad K_b = 2.2 \times 10^{-12}$$

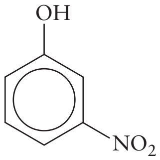
Calculate the pH of a 0.10 M aqueous solution of glycine at 25°C. (*Hint:* You may need to take account of the autoionization of water.)

114. Use the effect of steric hindrance to predict whether a tertiary amine should be a stronger base than ammonia in aqueous solution. (*Hint:* Assume that the effect of solvation is greater for ions than for neutral species.)

***115.** Consider the two following nitrophenol structures:



p-nitrophenol



m-nitrophenol

Predict which will be the stronger acid. (*Hint:* Consider possible resonance structures analogous to those given in the text for phenol.)

CUMULATIVE PROBLEMS

116. Use the data from Table 15.1, together with Le Châtelier's principle, to decide whether the autoionization of water is exothermic or endothermic.

117. Baking soda (sodium hydrogen carbonate, $NaHCO_3$) is used in baking because it reacts with acids in foods to form carbonic acid (H_2CO_3), which in turn decomposes to water and carbon dioxide. In a batter the carbon dioxide appears as gas bubbles that cause the bread or cake to rise.

(a) A rule of thumb in cooking is that $\frac{1}{2}$ teaspoon baking soda is neutralized by 1 cup of sour milk. The acid component of sour milk is lactic acid ($HC_3H_5O_3$). Write an equation for the neutralization reaction.

(b) If the density of baking soda is 2.16 g cm^{-3}, calculate the concentration of lactic acid in the sour milk, in moles per liter. Take 1 cup = 236.6 mL = 48 teaspoons.

(c) Calculate the volume of carbon dioxide that is produced at 1 atm pressure and 350°F (177°C) from the reaction of $\frac{1}{2}$ teaspoon of baking soda.

118. Boric acid, $B(OH)_3$, is an acid that acts differently from the usual Brønsted–Lowry acids. It reacts with water according to

$$B(OH)_3(aq) + 2\,H_2O(\ell) \rightleftharpoons B(OH)_4^-(aq) + H_3O^+(aq) \qquad K_a = 5.8 \times 10^{-10}$$

(a) Draw Lewis structures for $B(OH)_3$ and $B(OH)_4^-$. Can these be described as Lewis acids or Lewis bases?

(b) Calculate the pH of a 0.20 M solution of $B(OH)_3(aq)$.

119. At 40°C and 1.00 atm pressure, a gaseous monoprotic acid has a density of 1.05 g L^{-1}. After 1.85 g of this gas is dissolved in water and diluted to 450 mL, the pH is measured to be 5.01. Determine the K_a of this acid and use Table 15.2 to identify it.

120. At 25°C, the Henry's law constant for carbon dioxide dissolved in water is 1.8×10^3 atm. Calculate the pH of water saturated with $CO_2(g)$ at 25°C in Denver, where the barometric pressure is 0.833 atm.

CHAPTER 16

Solubility and Precipitation Equilibria

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Sodium acetate crystals ($NaC_2H_3O_2$) form quickly in a supersaturated solution when a small speck of solute is added.

Dissolution and precipitation are chemical reactions by which solids pass into and out of solution. A brief introduction and several examples appear in Chapter 11. These reactions involve equilibria between dissolved species and species in the solid state, and so are described by the general principles of chemical equilibrium in Chapter 14. These reactions rank alongside acid–base reactions in practical importance. The dissolution and reprecipitation of solids permit chemists to isolate single products from reaction mixtures and to purify impure solid samples. Understanding the mechanisms of these reactions helps engineers prevent formation of deposits in water processing and distribution systems and helps doctors reduce the incidence of painful kidney stones. Dissolution and precipitation control the formation of mineral deposits and profoundly affect the ecologies of rivers, lakes, and oceans.

Our theme throughout this chapter is to manipulate equilibria to control the solubilities of ionic solids. In the first section we describe general features of the equilibria that govern dissolution and precipitation. In the remaining sections we explore quantitative aspects of these equilibria, including the effects of additional solutes, of acids and bases, and of ligands that can bind to metal ions to form complex ions.

16.1 The Nature of Solubility Equilibria

General Features of Solubility Equilibria

Solubility equilibria resemble the equilibria between volatile liquids (or solids) and their vapors in a closed container. In both cases, particles from a condensed phase tend to escape and spread through a larger, but limited, volume. In both cases, equilibrium is a dynamic compromise in which the rate of escape of particles from the condensed phase is equal to their rate of return. In a vaporization–condensation equilibrium, we assumed that the vapor above the condensed phase was an ideal gas. The analogous starting assumption for a dissolution–precipitation reaction is that the solution above the undissolved solid is an ideal solution. A solution in which sufficient solute has been dissolved to establish a dissolution–precipitation equilibrium between the solid substance and its dissolved form is called a **saturated solution.**

Le Châtelier's principle applies to these equilibria, as it does to all equilibria. One way to exert a stress on a solubility equilibrium is to change the amount of solvent. Adding solvent reduces the concentration of dissolved substance; more solid then tends to dissolve to restore the concentration of the dissolved substance to its equilibrium value. If an excess of solvent is added so that all of the solid dissolves, then obviously the solubility equilibrium ceases to exist and the solution is **unsaturated.** In a vaporization–condensation equilibrium, this corresponds to the complete evaporation of the condensed phase. Removing solvent from an already saturated solution forces additional solid to precipitate in order to maintain a constant concentration. A volatile solvent is often removed by simply letting a solution stand uncovered until the solvent evaporates. When conditions are right, the solid forms as crystals on the bottom and sides of the container (Fig. 16.1).


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FIGURE 16.1 The beaker contains an aqueous solution of K_2PtCl_4, a substance used as a starting material in the synthesis of anticancer drugs. It is loosely covered to keep out dust and allowed to stand. As the water evaporates, the solution becomes saturated and deposits solid K_2PtCl_4 in the form of long, needle-like red crystals.

Controlled precipitation by manipulating solubility is a widely used technique for purifying reaction products in synthetic chemistry. Side reactions can generate significant amounts of impurities; other impurities enter with the starting materials or are put in deliberately to increase the reaction rate. Running a reaction may take only hours, but the *workup* (separation of crude product) and subsequent purification may require weeks. **Recrystallization,** one of the most powerful methods for purifying solids, relies on differences between the solubilities of the desired substance and its contaminants. An impure product is dissolved and reprecipitated, repeatedly if necessary, with careful control of the factors that influence solubility. Manipulating solubility requires an understanding of the equilibria that exist between an undissolved substance and its solution.

In recrystallization a solution begins to deposit a compound when it is brought to the point of saturation with respect to that compound. In dissolution the solvent attacks the solid and **solvates** it at the level of individual particles. In precipitation

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FIGURE 16.2 Vastly different quantities of different compounds will dissolve in 1 L of water at 20°C. Clockwise from the front are borax, potassium permanganate, lead(II) chloride, sodium phosphate decahydrate, calcium oxide, and potassium dichromate.

the reverse occurs: Solute-to-solute attractions are reestablished as the solute leaves the solution. Often, solute-to-solvent attractions persist right through the process of precipitation, and solvent incorporates itself into the solid. When lithium sulfate (Li_2SO_4) precipitates from water, it brings with it into the solid one molecule of water per formula unit:

$$2\,\text{Li}^+(aq) + \text{SO}_4^{2-}(aq) + \text{H}_2\text{O}(\ell) \longrightarrow \text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}(s)$$

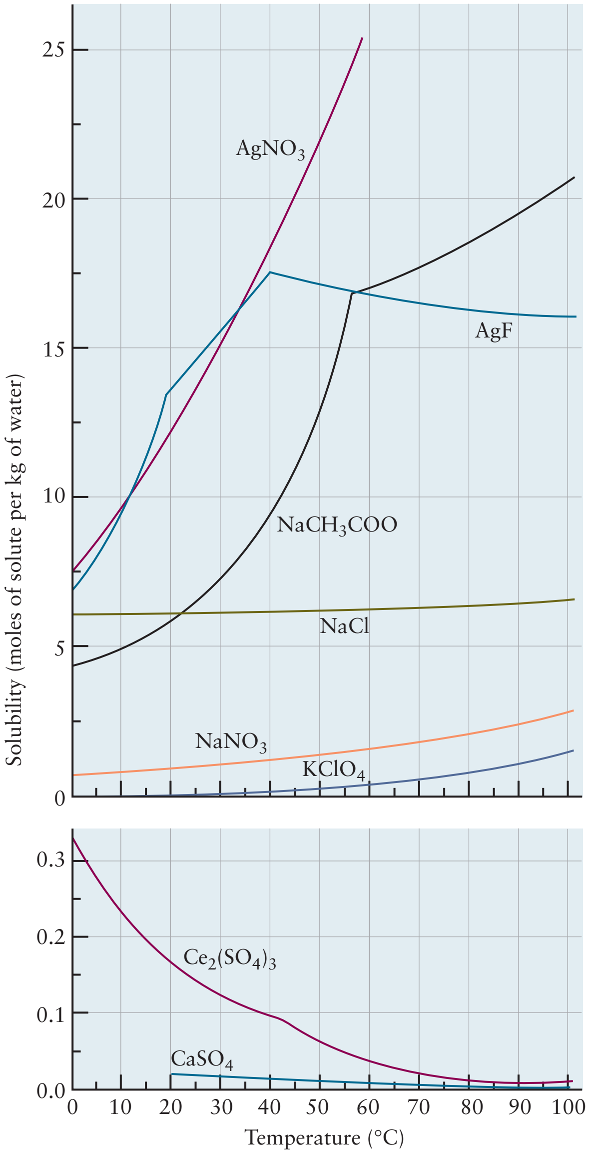
Such loosely bound solvent is known as solvent of crystallization (Fig. 2.1). Dissolving and then reprecipitating a compound may thus furnish material that has a different chemical formula and a different mass. Consequently, recrystallization processes for purification of reaction products must be planned carefully.

Dissolution–precipitation reactions frequently come to equilibrium slowly. Days or even weeks of shaking a solid in contact with a solvent may be required before the solution becomes saturated. Moreover, solutions sometimes become **supersaturated,** a condition in which the concentration of dissolved solid *exceeds* its equilibrium value. The delay, then, is in forming, not dissolving, the solid. A supersaturated solution may persist for months or years and require extraordinary measures to be brought to equilibrium, although thermodynamics shows that equilibrium is possible all along. The generally sluggish approach to equilibrium in dissolution–precipitation reactions is quite the opposite of the rapid rates at which acid–base reactions reach equilibrium.

The Solubility of Ionic Solids

The **solubility** of a substance in a solvent is defined as the greatest amount (expressed either in grams or in moles) that will dissolve in equilibrium in a specified volume of solvent at a particular temperature. Although solvents other than water are used in many applications, aqueous solutions are the most important and are the exclusive concern here. Salts show a wide range of solubilities in water (Fig. 16.2). Silver perchlorate ($AgClO_4$) dissolves to the remarkable extent of about 5570 g (or almost 27 mol) per liter of water at 25°C, but at the same temperature only about 0.0018 g (or 1.3×10^{-5} mol) of silver chloride (AgCl)

FIGURE 16.3 Most solubilities increase with increasing temperature, but some decrease. Note that the changes are not always smooth because different solid hydrates form over different temperature ranges.



dissolves per liter of water. Many salts with even lower solubilities are known. Solubilities often depend strongly on temperature (Fig. 16.3). Most dissolution reactions for ionic solids are endothermic (heat is absorbed), so by Le Châtelier's principle the solubility increases with increasing temperature. Those dissolution reactions that are exothermic (such as for $CaSO_4$) show the opposite behavior.

Although all ionic compounds dissolve to some extent in water, those having solubilities (at 25°C) of less than 0.1 g L^{-1} are called *insoluble*. Those having solubilities of more than 10 g L^{-1} are *soluble,* and the intermediate cases (0.1 to 10 g L^{-1}) are said to be *slightly soluble*. Fortunately, it is not necessary to memorize long lists of solubility data. Table 16.1 lists some generalizations concerning groups of salts and gives enough factual data to support good predictions about precipitation or dissolution in thousands of situations of practical importance. Knowing the solubilities of ionic substances, even in these qualitative terms, provides a way to predict the courses of numerous reactions. For example, when a solution of KI is added to one of $Pb(NO_3)_2$, K^+ and NO_3^- ions are brought into contact, as are Pb^{2+} and I^- ions. From the table, KNO_3 is a soluble salt but PbI_2 is insoluble; therefore, a precipitate of PbI_2 will appear (Fig. 16.4).


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FIGURE 16.4 A yellow precipitate of lead iodide forms when a drop of KI solution is added to a solution of $Pb(NO_3)_2$.

TABLE 16.1 Solubilities of Ionic Compounds in Water

Anion	Soluble[†]	Slightly Soluble	Insoluble
NO_3^- (nitrate)	All	—	—
CH_3COO^- (acetate)	Most	—	$Be(CH_3COO)_2$
ClO_3^- (chlorate)	All	—	—
ClO_4^- (perchlorate)	Most	$KClO_4$	—
F^- (fluoride)	Group I, AgF, BeF_2	SrF_2, BaF_2, PbF_2	MgF_2, CaF_2
Cl^- (chloride)	Most	$PbCl_2$	AgCl, Hg_2Cl_2
Br^- (bromide)	Most	$PbBr_2$, $HgBr_2$	AgBr, Hg_2Br_2
I^- (iodide)	Most	—	AgI, Hg_2I_2, PbI_2, HgI_2
SO_4^{2-} (sulfate)	Most	$CaSO_4$, Ag_2SO_4, Hg_2SO_4	$SrSO_4$, $BaSO_4$, $PbSO_4$
S^{2-} (sulfide)	Groups I and II, $(NH_4)_2S$	—	Most
CO_3^{2-} (carbonate)	Group I, $(NH_4)_2CO_3$	—	Most
SO_3^{2-} (sulfite)	Group I, $(NH_4)_2SO_3$	—	Most
PO_4^{3-} (phosphate)	Group I, $(NH_4)_3PO_4$	—	Most
OH^- (hydroxide)	Group I, $Ba(OH)_2$	$Sr(OH)_2$, $Ca(OH)_2$	Most

[†] Soluble compounds are defined as those that dissolve to the extent of 10 or more grams per liter; slightly soluble compounds, 0.1 to 10 grams per liter; and insoluble compounds, less than 0.1 gram per liter at room temperature.

16.2 Ionic Equilibria between Solids and Solutions

When an ionic solid such as CsCl dissolves in water, it breaks up into ions that move apart from each other and become solvated by water molecules (*aquated*, or *hydrated;* Fig. 16.5). The aquated ions are shown in the chemical equation for the solubility equilibrium. Thus,

$$\mathrm{CsCl}(s) \rightleftharpoons \mathrm{Cs}^+(aq) + \mathrm{Cl}^-(aq)$$

shows that the dissolved particles are ions. For a highly soluble salt (such as CsCl), the concentrations of the ions in a saturated aqueous solution are so large that the solution is nonideal. There is much association among the ions in solution, resulting in temporary pairs of oppositely charged ions and in larger clusters as well. In such cases the simple type of equilibrium expression developed in Sections 14.2 and 14.3 does not apply; therefore, we restrict our attention to sparingly soluble and "insoluble" salts, for which the concentrations in a saturated solution are 0.1 mol L^{-1} or less—low enough that the interactions among the solvated ions are relatively small.

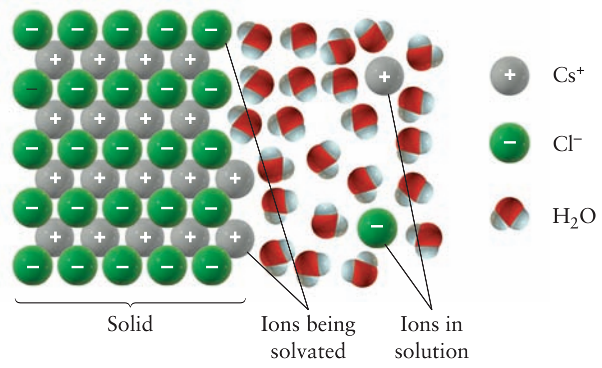

FIGURE 16.5 The dissolution of the ionic solid CsCl in water. Note the different solvations of positive and negative ions. Water molecules arrange themselves so the negative ends of their dipoles (the oxygen atoms) point toward the positively charged Cs^+ ions. The water molecules form hydrogen bonds to the Cl^- anions, so the O—H—Cl atoms line nearly in a straight line.

The sparingly soluble salt silver chloride, for example, establishes the following equilibrium when placed in water:

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

The equilibrium law for this reaction (written by following the rules for heterogeneous equilibria from Sections 14.2 and 14.3) is

$$[\mathrm{Ag}^+][\mathrm{Cl}^-] = K_{\mathrm{sp}}$$

where the subscript "sp," standing for **"solubility product,"** distinguishes the K as referring to the dissolution of a slightly soluble ionic solid in water. At 25°C, K_{sp} has the numerical value 1.6×10^{-10} for silver chloride. In the AgCl solubility product expression, the concentrations of the two ions produced are raised to the first power because their coefficients are 1 in the chemical equation. Solid AgCl does not appear in the equilibrium expression; the amount of pure solid AgCl does not affect the equilibrium as long as *some* is present. If *no* solid is present, then the product of the two ion concentrations is no longer constrained by the solubility product expression.

Solubility and K_{sp}

The molar solubility of a salt in water is not the same as its solubility product constant, but a simple relation often exists between them. For example, let's define S

TABLE 16.2 Solubility Product Constants K_{sp} at 25°C

Iodates	
$AgIO_3$	$[Ag^+][IO_3^-] = 3.1 \times 10^{-8}$
$CuIO_3$	$[Cu^+][IO_3^-] = 1.4 \times 10^{-7}$
$Pb(IO_3)_2$	$[Pb^{2+}][IO_3^-]^2 = 2.6 \times 10^{-13}$
Carbonates	
Ag_2CO_3	$[Ag^+]^2[CO_3^{2-}] = 6.2 \times 10^{-12}$
$BaCO_3$	$[Ba^{2+}][CO_3^{2-}] = 8.1 \times 10^{-9}$
$CaCO_3$	$[Ca^{2+}][CO_3^{2-}] = 8.7 \times 10^{-9}$
$PbCO_3$	$[Pb^{2+}][CO_3^{2-}] = 3.3 \times 10^{-14}$
$MgCO_3$	$[Mg^{2+}][CO_3^{2-}] = 4.0 \times 10^{-5}$
$SrCO_3$	$[Sr^{2+}][CO_3^{2-}] = 1.6 \times 10^{-9}$
Chromates	
Ag_2CrO_4	$[Ag^+]^2[CrO_4^{2-}] = 1.9 \times 10^{-12}$
$BaCrO_4$	$[Ba^{2+}][CrO_4^{2-}] = 2.1 \times 10^{-10}$
$PbCrO_4$	$[Pb^{2+}][CrO_4^{2-}] = 1.8 \times 10^{-14}$
Oxalates	
CuC_2O_4	$[Cu^{2+}][C_2O_4^{2-}] = 2.9 \times 10^{-8}$
FeC_2O_4	$[Fe^{2+}][C_2O_4^{2-}] = 2.1 \times 10^{-7}$
MgC_2O_4	$[Mg^{2+}][C_2O_4^{2-}] = 8.6 \times 10^{-5}$
PbC_2O_4	$[Pb^{2+}][C_2O_4^{2-}] = 2.7 \times 10^{-11}$
SrC_2O_4	$[Sr^{2+}][C_2O_4^{2-}] = 5.6 \times 10^{-8}$
Sulfates	
$BaSO_4$	$[Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$
$CaSO_4$	$[Ca^{2+}][SO_4^{2-}] = 2.4 \times 10^{-5}$
$PbSO_4$	$[Pb^{2+}][SO_4^{2-}] = 1.1 \times 10^{-8}$
Fluorides	
BaF_2	$[Ba^{2+}][F^-]^2 = 1.7 \times 10^{-6}$
CaF_2	$[Ca^{2+}][F^-]^2 = 3.9 \times 10^{-11}$
MgF_2	$[Mg^{2+}][F^-]^2 = 6.6 \times 10^{-9}$
PbF_2	$[Pb^{2+}][F^-]^2 = 3.6 \times 10^{-8}$
SrF_2	$[Sr^{2+}][F^-]^2 = 2.8 \times 10^{-9}$
Chlorides	
$AgCl$	$[Ag^+][Cl^-] = 1.6 \times 10^{-10}$
$CuCl$	$[Cu^+][Cl^-] = 1.0 \times 10^{-6}$
Hg_2Cl_2	$[Hg_2^{2+}][Cl^-]^2 = 2 \times 10^{-18}$
Bromides	
$AgBr$	$[Ag^+][Br^-] = 7.7 \times 10^{-13}$
$CuBr$	$[Cu^+][Br^-] = 4.2 \times 10^{-8}$
Hg_2Br_2	$[Hg_2^{2+}][Br^-]^2 = 1.3 \times 10^{-21}$
Iodides	
AgI	$[Ag^+][I^-] = 1.5 \times 10^{-16}$
CuI	$[Cu^+][I^-] = 5.1 \times 10^{-12}$
PbI_2	$[Pb^{2+}][I^-]^2 = 1.4 \times 10^{-8}$
Hg_2I_2	$[Hg_2^{2+}][I^-]^2 = 1.2 \times 10^{-28}$
Hydroxides	
$AgOH$	$[Ag^+][OH^-] = 1.5 \times 10^{-8}$
$Al(OH)_3$	$[Al^{3+}][OH^-]^3 = 3.7 \times 10^{-15}$
$Fe(OH)_3$	$[Fe^{3+}][OH^-]^3 = 1.1 \times 10^{-36}$
$Fe(OH)_2$	$[Fe^{2+}][OH^-]^2 = 1.6 \times 10^{-14}$
$Mg(OH)_2$	$[Mg^{2+}][OH^-]^2 = 1.2 \times 10^{-11}$
$Mn(OH)_2$	$[Mn^{2+}][OH^-]^2 = 2 \times 10^{-13}$
$Zn(OH)_2$	$[Zn^{2+}][OH^-]^2 = 4.5 \times 10^{-17}$

as the molar solubility of AgCl(s) in water at 25°C. Then, from stoichiometry, $[Ag^+] = [Cl^-] = S$ is the molarity of either ion at equilibrium. Hence,

$$[Ag^+][Cl^-] = S^2 = K_{sp} = 1.6 \times 10^{-10}$$

Taking the square roots of both sides of the equation gives

$$S = 1.26 \times 10^{-5}\ \text{M}$$

which rounds off to 1.3×10^{-5} M. This is the molar solubility of AgCl in water. It is converted to a gram solubility by multiplying by the molar mass of AgCl:

$$(1.26 \times 10^{-5}\ \text{mol L}^{-1})(143.3\ \text{g mol}^{-1}) = 1.8 \times 10^{-3}\ \text{g L}^{-1}$$

Therefore, 1.8×10^{-3} g of AgCl dissolves per liter of water at 25°C.

Solubility product constants (like solubilities) can be sensitive to temperature. At 100°C the K_{sp} for silver chloride is 2.2×10^{-8}; hot water dissolves about 12 times as much silver chloride as does water at 25°C. Refer to Table 16.2 for the solubility product constants at 25°C of a number of important sparingly soluble salts.

EXAMPLE 16.1

The K_{sp} of calcium fluoride is 3.9×10^{-11}. Calculate the concentrations of calcium and fluoride ions in a saturated solution of CaF_2 at 25°C, and determine the solubility of CaF_2 in grams per liter.

SOLUTION

The solubility equilibrium is

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ F^-(aq)$$

and the expression for the solubility product is

$$[Ca^{2+}][F^-]^2 = K_{sp}$$

The concentration of fluoride ion is squared because it has a coefficient of 2 in the chemical equation.

If S mol of CaF_2 dissolves in 1 L, the equilibrium concentration of Ca^{2+} will be $[Ca^{2+}] = S$. The concentration of F^- will be $[F^-] = 2S$, because each mole of CaF_2 produces *two* moles of fluoride ions. Therefore,

$$[Ca^{2+}][F^-]^2 = S \times (2S)^2 = 4S^3 = K_{sp} = 3.9 \times 10^{-11}$$

Solving for S^3 gives

$$S^3 = \tfrac{1}{4}(3.9 \times 10^{-11})$$

Taking the cube roots of both sides of this equation gives

$$S = 2.1 \times 10^{-4}$$

The equilibrium concentrations are therefore

$$[Ca^{2+}] = S = 2.1 \times 10^{-4}\ \text{M}$$

$$[F^-] = 2S = 4.3 \times 10^{-4}\ \text{M}$$

Because the molar mass of CaF_2 is 78.1 g mol^{-1}, the gram solubility is

$$\text{gram solubility} = (2.1 \times 10^{-4}\ \text{mol L}^{-1})(78.1\ \text{g mol}^{-1}) = 0.017\ \text{g L}^{-1}$$

Related Problems: 7, 8, 9, 10, 11, 12

It is possible to reverse the procedure just outlined, of course, and determine the value of K_{sp} from measured solubilities, as the following example illustrates.

EXAMPLE 16.2

Silver chromate (Ag_2CrO_4) is a red solid that dissolves in water to the extent of 0.029 g L^{-1} at 25°C. Estimate its K_{sp} and compare your estimate with the value in Table 16.2.

SOLUTION

The molar solubility is calculated from the gram solubility and the molar mass of silver chromate (331.73 g mol^{-1}):

$$\text{molar solubility} = \frac{0.029 \text{ g L}^{-1}}{331.73 \text{ g mol}^{-1}} = 8.74 \times 10^{-5} \text{ mol L}^{-1}$$

An extra significant digit is carried in this intermediate result to avoid round-off errors. Because each mole of Ag_2CrO_4 that dissolves gives *two* moles of silver ion, the concentration of $Ag^+(aq)$ is

$$[Ag^+] = 2 \times 8.74 \times 10^{-5} \text{ M} = 1.75 \times 10^{-4} \text{ M}$$

and that of CrO_4^{2-} is simply 8.74×10^{-5} M. The solubility product constant is then

$$\begin{aligned} K_{sp} = \; & [Ag^+]^2[CrO_4^{2-}] = (1.75 \times 10^{-4})^2 \times (8.74 \times 10^{-5}) \\ & = 2.7 \times 10^{-12} \end{aligned}$$

This estimate is about 42% greater than the tabulated value, 1.9×10^{-12}.

Related Problems: 13, 14, 15, 16

Computing K_{sp} from a solubility and solubility from K_{sp} is valid if the solution is ideal and if there are no side reactions that reduce the concentrations of the ions after they enter solution. If such reactions are present, they cause higher solubilities than are predicted from the K_{sp} expression. For example, the solubility computed for $PbSO_4(s)$ at 25°C from its K_{sp} is 0.032 g L^{-1}, whereas that measured experimentally is 0.0425 g L^{-1}. The difference is caused by the presence of species other than $Pb^{2+}(aq)$ in solution, such as $PbOH^+(aq)$. Further discussion of these side reactions is deferred to Section 16.6.

16.3 Precipitation and the Solubility Product

So far, we have considered only cases in which a single slightly soluble salt attains equilibrium with its component ions in water. The relative concentrations of the cations and anions in such solutions echo their relative numbers of moles in the original salt. Thus, when AgCl is dissolved, equal numbers of moles of $Ag^+(aq)$ and $Cl^-(aq)$ ions result, and when Ag_2SO_4 is dissolved, twice as many moles of $Ag^+(aq)$ ions as $SO_4^{2-}(aq)$ are produced. A solubility product relationship such as

$$[Ag^+][Cl^-] = K_{sp}$$

is more general than this, however, and continues in force even if the relative number of moles of the two ions in solution differ from those in the pure solid compound. Such a situation often results when two solutions are mixed to give a precipitate or when another salt is present that contains an ion common to the salt under consideration.

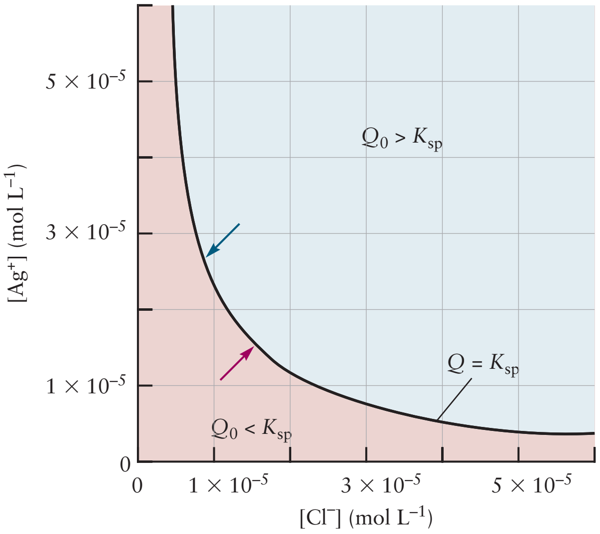

FIGURE 16.6 Some solid silver chloride is in contact with a solution containing $Ag^+(aq)$ and $Cl^-(aq)$ ions. If a solubility equilibrium exists, then the product Q of the concentrations of the ions $[Ag^+] \times [Cl^-]$ is a constant, K_{sp} (curved line). When Q exceeds K_{sp}, solid silver chloride tends to precipitate until equilibrium is attained. When Q is less than K_{sp}, additional solid tends to dissolve. If no solid is present, Q remains less than K_{sp}.

Precipitation from Solution

Suppose a solution is prepared by mixing one soluble salt, such as $AgNO_3$, with a solution of a second, such as NaCl. Will a precipitate of very slightly soluble silver chloride form? To reach an answer, the reaction quotient Q that was defined in connection with gaseous equilibria (see Section 14.6) is used. The initial reaction quotient Q_0, when the mixing of the solutions is complete but before any reaction occurs, is

$$Q_0 = [Ag^+]_0[Cl^-]_0$$

If $Q_0 < K_{sp}$, no solid silver chloride can appear. On the other hand, if $Q_0 > K_{sp}$, solid silver chloride precipitates until the reaction quotient Q reaches K_{sp} (Fig. 16.6).

EXAMPLE 16.3

An emulsion of silver chloride for photographic film is prepared by adding a soluble chloride salt to a solution of silver nitrate. Suppose 500 mL of a solution of $CaCl_2$ with a chloride ion concentration of 8.0×10^{-6} M is added to 300 mL of a 0.0040 M solution of $AgNO_3$. Will a precipitate of AgCl(*s*) form when equilibrium is reached?

SOLUTION

The "initial concentrations" to be used in calculating Q_0 are those *before* reaction but *after* dilution through mixing the two solutions. The initial concentration of $Ag^+(aq)$ after dilution from 300 mL to 800 mL of solution is

$$[Ag^+]_0 = 0.00400 \text{ M} \times \left(\frac{300 \text{ mL}}{800 \text{ mL}}\right) = 0.0015 \text{ M}$$

and that of $Cl^-(aq)$ is

$$[Cl^-]_0 = 8.0 \times 10^{-6} \text{ M} \times \left(\frac{500 \text{ mL}}{800 \text{ mL}}\right) = 5.0 \times 10^{-6} \text{ M}$$

The initial reaction quotient is

$$Q_0 = [Ag^+]_0[Cl^-]_0 = (0.0015)(5.0 \times 10^{-6}) = 7.5 \times 10^{-9}$$

Because $Q_0 > K_{sp}$, a precipitate of silver chloride appears at equilibrium, although there may be too little to detect visually. Another possible precipitate, calcium nitrate, is far too soluble to form in this experiment (see Table 16.1).

Related Problems: 17, 18, 19, 20

The equilibrium concentrations of ions after the mixing of two solutions to give a precipitate are most easily calculated by supposing that the reaction first goes to completion (consuming one type of ion) and that subsequent dissolution of the solid restores some of that ionic species to solution—just the approach used in Example 15.8 for the addition of a strong acid to a buffer solution.

EXAMPLE 16.4

Calculate the equilibrium concentrations of silver and chloride ions resulting from the precipitation reaction of Example 16.3.

SOLUTION

In this case the silver ion is clearly in excess; therefore, the chloride ion is the limiting reactant. If all of it were used up to make solid AgCl, the concentration of the remaining silver ion would be

$$[Ag^+] = 0.0015 - 5.0 \times 10^{-6} = 0.0015 \text{ M}$$

Set up the equilibrium calculation as

	$AgCl(s) \rightleftharpoons Ag^+(aq)$	$+ Cl^-(aq)$
Initial concentration (M)	0.0015	0
Change in concentration (M)	$+y$	$+y$
Equilibrium concentration (M)	$0.0015 + y$	y

so that the equilibrium expression is

$$(0.0015 + y)y = K_{sp} = 1.6 \times 10^{-10}$$

This quadratic equation can be solved by use of the quadratic formula, provided the calculator carries ten significant figures. It can be solved more easily by making the approximation that y is much smaller than 0.0015; the equation therefore simplifies to

$$0.0015y \approx 1.6 \times 10^{-10}$$

$$y \approx 1.1 \times 10^{-7} \text{ M} = [Cl^-]$$

The assumption about the size of y was justified. The concentration of silver ion is

$$[Ag^+] = 0.0015 \text{ M}$$

Related Problems: 21, 22, 23, 24

The Common-Ion Effect

Suppose a small amount of NaCl(s) is added to a saturated solution of AgCl. What happens? Sodium chloride is quite soluble in water and dissolves to form $Na^+(aq)$ and $Cl^-(aq)$ ions, raising the concentration of chloride ion. The quantity $Q_0 = [Ag^+][Cl^-]$ then exceeds the K_{sp} of silver chloride, and silver chloride precipitates until the concentrations of $Ag^+(aq)$ and $Cl^-(aq)$ are sufficiently reduced that the solubility product expression once again is satisfied.

The same equilibrium may be approached from the other direction. The amount of AgCl(s) that can dissolve in a solution of sodium chloride is less than the amount that could dissolve in the same volume of pure water. Because $[Ag^+][Cl^-] = K_{sp}$, a graph of the equilibrium concentration of silver ion against chloride concentration has the form of a hyperbola (Fig. 16.7). The presence of excess $Cl^-(aq)$ reduces the concentration of $Ag^+(aq)$ permitted, and the solubility

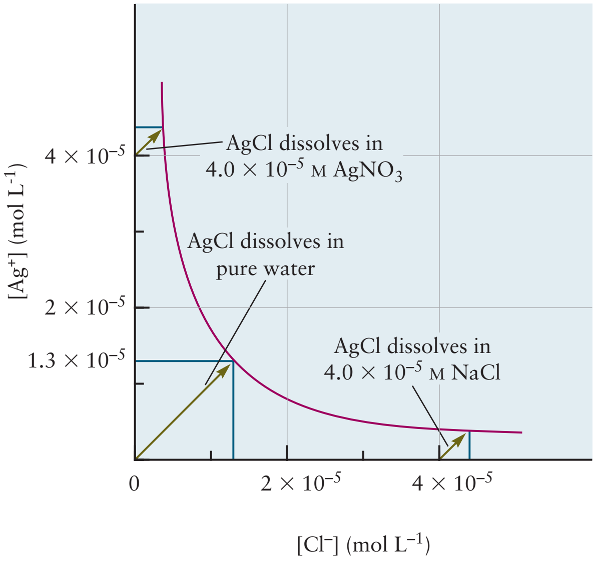

FIGURE 16.7 The presence of a dissolved common ion reduces the solubility of a salt in solution. As the AgCl dissolves, the concentrations of the ions follow the paths shown by the green arrows until they reach the red equilibrium curve. The molar solubilities are proportional to the lengths of the blue lines: 1.3×10^{-5} mol L^{-1} for AgCl in pure water, but only 0.37×10^{-5} mol L^{-1} in either 4.0×10^{-5} M $AgNO_3$ or 4.0×10^{-5} M NaCl.

of AgCl(*s*) is reduced. In the same way, the prior presence of $Ag^+(aq)$ in the solvent (for example, when an attempt is made to dissolve AgCl in water that already contains $AgNO_3$) reduces the amount of $Cl^-(aq)$ permitted at equilibrium and also reduces the solubility of AgCl. This is referred to as the **common-ion effect:** If the solution and the solid salt to be dissolved in it have an ion in common, then the solubility of the salt is depressed.

Let's examine the quantitative consequences of the common-ion effect. Suppose an excess of AgCl(*s*) is added to 1.00 L of a 0.100 M NaCl solution and the solubility is again determined. If S mol of AgCl dissolves per liter, the concentration of $Ag^+(aq)$ will be S mol L^{-1} and that of $Cl^-(aq)$ will be

$$[Cl^-] = 0.100 + S$$

because the chloride ion comes from two sources: the 0.100 M NaCl and the dissolution of AgCl. The expression for the solubility product is written as

$$[Ag^+][Cl^-] = S(0.100 + S) = K_{sp} = 1.6 \times 10^{-10}$$

The solubility of AgCl(*s*) in this solution must be smaller than it is in pure water, which is much smaller than 0.100. That is,

$$S < 1.3 \times 10^{-5} \ll 0.100$$

Thus, $(0.100 + S)$ can be approximated by 0.100 (as in Example 16.4), giving

$$(0.100)S \approx 1.6 \times 10^{-10}$$

$$S \approx 1.6 \times 10^{-9}$$

This is indeed much smaller than 0.100, so the approximation was a very good one. Therefore, at equilibrium,

$$[Ag^+] = S = 1.6 \times 10^{-9} \text{ M}$$

$$[Cl^-] = 0.100 \text{ M}$$

The gram solubility of AgCl in this example is

$$(1.6 \times 10^{-9} \text{ mol L}^{-1})(143.3 \text{ g mol}^{-1}) = 2.3 \times 10^{-7} \text{ g L}^{-1}$$

The solubility of AgCl in 0.100 M NaCl is lower than that in pure water by a factor of about 8000.

EXAMPLE 16.5

What is the gram solubility of $CaF_2(s)$ in a 0.100 M solution of NaF?

SOLUTION

Again, the molar solubility is denoted by S. The only source of the $Ca^{2+}(aq)$ in the solution at equilibrium is the dissolution of CaF_2, whereas the $F^-(aq)$ has two sources, the CaF_2 and the NaF. Hence,

	$CaF_2(s) \rightleftharpoons Ca^{2+}(aq)$	+	$2\,F^-(aq)$
Initial concentration (M)	0		0.100
Change in concentration (M)	$+S$		$+2S$
Equilibrium concentration (M)	S		$0.100 + 2S$

If $0.100 + 2S$ is approximated as 0.100, then

$$[Ca^{2+}][F^-]^2 = K_{sp}$$

$$S(0.100)^2 = 3.9 \times 10^{-11}$$

$$S = 3.9 \times 10^{-9}$$

Clearly,

$$2S = 7.8 \times 10^{-9} \ll 0.100$$

so the assumption was justified. The gram solubility of CaF_2 is

$$(3.9 \times 10^{-9} \text{ mol L}^{-1})(78.1 \text{ g mol}^{-1}) = 3.0 \times 10^{-7} \text{ g L}^{-1}$$

and the solubility in this case is reduced by a factor of 50,000.

Related Problems: 25, 26, 27, 28

16.4 The Effects of pH on Solubility

Some solids are only weakly soluble in water but dissolve readily in acidic solutions. Copper and nickel sulfides from ores, for example, can be brought into solution with strong acids, a fact that aids greatly in the separation and recovery of these valuable metals in their elemental forms. The effect of pH on solubility is shown dramatically in the damage done to buildings and monuments by acid precipitation (Fig. 16.8). Both marble and limestone are made up of small crystals of calcite ($CaCO_3$), which dissolves to only a limited extent in "natural" rain (with a pH of about 5.6) but dissolves much more extensively as the rainwater becomes more acidic. The reaction

$$CaCO_3(s) + H_3O^+(aq) \longrightarrow Ca^{2+}(aq) + HCO_3^-(aq) + H_2O(\ell)$$

causes this increase. This section examines the role of pH in solubility.

Solubility of Hydroxides

One direct effect of pH on solubility occurs with the metal hydroxides. The concentration of OH^- appears explicitly in the expression for the solubility product of such compounds. Thus, for the dissolution of $Zn(OH)_2(s)$,

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2\,OH^-(aq)$$

the solubility product expression is

$$[Zn^{2+}][OH^-]^2 = K_{sp} = 4.5 \times 10^{-17}$$

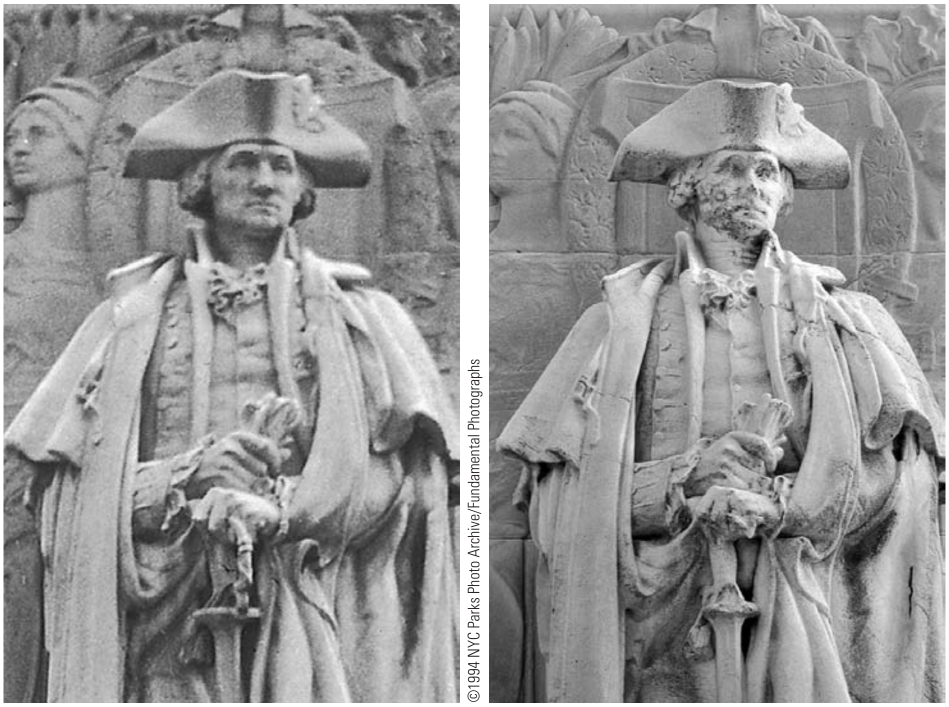

FIGURE 16.8 The calcium carbonate in marble and limestone is very slightly soluble in neutral water. Its solubility is much greater in acidic water. Objects carved of these materials dissolve relatively rapidly in areas where rain, snow, or fog is acidified from air pollution. Shown here is the damage to a marble statue of George Washington between 1935 (left) and 1994 (right).

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As the solution is made more acidic, the concentration of hydroxide ion decreases, causing an increase in the concentration of $Zn^{2+}(aq)$ ion. Zinc hydroxide is thus more soluble in acidic solution than in pure water.

EXAMPLE 16.6

Compare the solubility of $Zn(OH)_2$ in pure water with that in a solution buffered at pH 6.00.

SOLUTION

In pure water the usual solubility product calculation applies:

$$[Zn^{2+}] = S \qquad [OH^-] = 2S$$

$$S(2S)^2 = 4S^3 = K_{sp} = 4.5 \times 10^{-17}$$

$$S = 2.2 \times 10^{-6}\ \text{M} = [Zn^{2+}]$$

so the solubility is 2.2×10^{-6} mol L^{-1}, or 2.2×10^{-4} g L^{-1}. Using

$$[OH^-] = 2S = 4.5 \times 10^{-6}\ \text{M}$$

the resulting solution is found to have pH 8.65.

In the second case it is assumed that the solution is buffered sufficiently that the pH remains 6.00 after dissolution of the zinc hydroxide. Then

$$[OH^-] = 1.0 \times 10^{-8}\ \text{M}$$

$$[Zn^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{4.5 \times 10^{-17}}{(1.0 \times 10^{-8})^2} = 0.45\ \text{M}$$

so that 0.45 mol L^{-1}, or 45 g L^{-1}, should dissolve in this case. When ionic concentrations are this high, the simple form of the solubility expression will likely break down, but the qualitative conclusion is still valid: $Zn(OH)_2$ is far more soluble at pH 6.00 than in pure water.

Related Problems: 31, 32

Solubility of Salts of Bases

Metal hydroxides can be described as salts of a strong base, the hydroxide ion. The solubility of salts in which the anion is a different weak or strong base is also affected by pH. For example, consider a solution of a slightly soluble fluoride, such as calcium fluoride. The solubility equilibrium is

$$\mathrm{CaF_2}(s) \rightleftharpoons \mathrm{Ca^{2+}}(aq) + 2\,\mathrm{F^-}(aq) \qquad K_{\mathrm{sp}} = 3.9 \times 10^{-11}$$

As the solution is made more acidic, some of the fluoride ion reacts with hydronium ion through

$$\mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq) \rightleftharpoons \mathrm{HF}(aq) + \mathrm{H_2O}(\ell)$$

Because this is just the reverse of the acid ionization of HF, its equilibrium constant is the reciprocal of K_a for HF, or $1/(3.5 \times 10^{-4}) = 2.9 \times 10^3$. As acid is added, the concentration of fluoride ion is reduced, so the calcium ion concentration must increase to maintain the solubility product equilibrium for CaF_2. As a result, the solubility of fluoride salts increases in acidic solution. The same applies to other ionic substances in which the anion is a weak or a strong base. By contrast, the solubility of a salt such as AgCl is only very slightly affected by a decrease in pH. The reason is that HCl is a strong acid, so Cl^- is ineffective as a base. The reaction

$$\mathrm{Cl^-}(aq) + \mathrm{H_3O^+}(aq) \longrightarrow \mathrm{HCl}(aq) + \mathrm{H_2O}(\ell)$$

occurs to a negligible extent in acidic solution.

A DEEPER LOOK

16.5 Selective Precipitation of Ions

One way to analyze a mixture of ions in solution is to separate the mixture into its components by exploiting the differences in the solubilities of compounds containing the ions. To separate silver ions from lead ions, for example, a search is made for compounds of these elements that (1) have a common anion and (2) have widely different solubilities. The chlorides AgCl and $PbCl_2$ are two such compounds, for which the solubility equilibria are

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \qquad K_{\mathrm{sp}} = 1.6 \times 10^{-10}$$

$$\mathrm{PbCl_2}(s) \rightleftharpoons \mathrm{Pb^{2+}}(aq) + 2\,\mathrm{Cl^-}(aq) \qquad K_{\mathrm{sp}} = 2.4 \times 10^{-4}$$

Lead chloride is far more soluble in water than is silver chloride. Consider a solution that is 0.10 M in both Ag^+ and Pb^{2+}. Is it possible to add enough Cl^- to precipitate almost all the Ag^+ ions but leave all the Pb^{2+} ions in solution? If so, a quantitative separation of the two species can be achieved.

For Pb^{2+} to remain in solution, its reaction quotient must remain smaller than K_{sp}: $Q = [\mathrm{Pb^{2+}}][\mathrm{Cl^-}]^2 < K_{sp}$. Inserting K_{sp} and the concentration of Pb^{2+} gives

$$[\mathrm{Cl^-}]^2 < \frac{K_{\mathrm{sp}}}{[\mathrm{Pb^{2+}}]} = \frac{2.4 \times 10^{-4}}{0.10} = 2.4 \times 10^{-3}$$

The square root of this is

$$[\mathrm{Cl^-}] < 4.9 \times 10^{-2}\ \mathrm{M}$$

Thus, as long as the chloride ion concentration remains smaller than 0.049 M, no $PbCl_2$ should precipitate. To reduce the *silver* ion concentration in solution as far as possible (that is, to precipitate out as much silver chloride as possible), the chloride ion concentration should be kept as high as possible without exceeding 0.049 M. If exactly this concentration of $Cl^-(aq)$ is chosen, then at equilibrium,

$$[\mathrm{Ag^+}] = \frac{K_{\mathrm{sp}}}{[\mathrm{Cl^-}]} = \frac{1.6 \times 10^{-10}}{0.049} = 3.3 \times 10^{-9}$$

At that concentration of Cl^-, the concentration of Ag^+ has been reduced to 3.3×10^{-9} from the original concentration of 0.10 M. In other words, only about three Ag^+ ions in 10^8 remain in solution, but all the Pb^{2+} ions are left in solution. A nearly perfect separation of the two ionic species has been achieved.

This calculation gave the optimal theoretical separation factor for the two ions. In practice it is necessary to keep the chloride concentration lower. If $[Cl^-]$ is ten times smaller, or 0.0049 M, about three Ag^+ ions in 10^7 remain in solution with the Pb^{2+}. This is ten times more Ag^+ than if $[Cl^-] = 0.049$ M, but the separation of Ag^+ from Pb^{2+} is still very good.

Figure 16.9 shows graphically how ions can be separated based on solubility. The relation between the concentration of Pb^{2+} and Cl^- ions in contact with solid $PbCl_2$

$$[\mathrm{Pb^{2+}}] = \frac{K_{\mathrm{sp}}}{[\mathrm{Cl^-}]^2}$$

can be rewritten in a useful form by taking the common base-10 logarithms of both sides:

$$\log_{10}[\mathrm{Pb^{2+}}] = -2\log_{10}[\mathrm{Cl^-}] + \log_{10}K_{\mathrm{sp}}$$

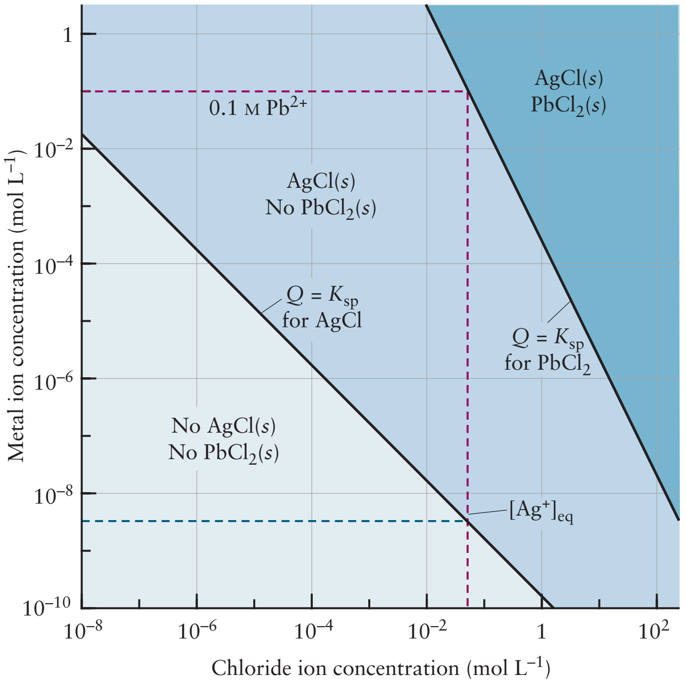

FIGURE 16.9 To separate a mixture of Ag^+ and Pb^{2+} ions, a chloride ion concentration is selected that gives a Pb^{2+} concentration below the equilibrium curve for $PbCl_2$ (so all Pb^{2+} remains in solution) but well above the equilibrium curve for Ag^+. As a result, nearly all the Ag^+ precipitates as AgCl. If $[Pb^{2+}]_0 = [Ag^+]_0 = 0.1$ M, then the maximum $[Cl^-]$ is found by tracing the horizontal red line and then dropping down the vertical red line to find $[Cl^-] = 0.049$ M. The concentration of Ag^+ still in solution is found by tracing the horizontal blue line from the intersection of the $[Cl^-]$ line of the AgCl equilibrium curve back to the vertical axis where $[Ag^+] = 3.3 \times 10^{-9}$ M.

That is, a graph of $\log_{10} [Pb^{2+}]$ against $\log_{10} [Cl^-]$ is a straight line with slope −2. The corresponding graph for the AgCl solubility equilibrium has slope −1.

$$\log_{10}[Ag^+] = -\log_{10}[Cl^-] + \log_{10}K_{sp}$$

If the concentration of Cl^- and the initial concentrations of the metal ions correspond to a point that lies between the two lines in Figure 16.9, then AgCl precipitates but $PbCl_2$ does not.

Metal Sulfides

Controlling the solubility of metal sulfides has important applications. According to Table 16.2, most metal sulfides are very slightly soluble in water; only a very small amount of a compound such as ZnS(*s*) will dissolve in water. Although it is tempting to write the resulting equilibrium as

$$ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq) \qquad K_{sp} = ?$$

in analogy with the equilibria for other weakly soluble salts, this is misleading, because S^{2-}, like O^{2-}, is a very strong base (stronger than OH^-) and reacts almost quantitatively with water.

$$S^{2-}(aq) + H_2O(\ell) \longrightarrow HS^-(aq) + OH^-(aq)$$

TABLE 16.3 Equilibrium Constants for Metal Sulfide Dissolution at 25°C

Metal Sulfide	$K^{\dagger}$
CuS	5×10^{-37}
PbS	3×10^{-28}
CdS	7×10^{-28}
SnS	9×10^{-27}
ZnS	2×10^{-25}
FeS	5×10^{-19}
MnS	3×10^{-14}

†*K* is the equilibrium constant for the reaction $MS(s) + H_2O(\ell) \rightleftharpoons M^{2+}(aq) + OH^-(aq) + HS^-(aq)$.

Recent research has shown that K_b for this reaction is on the order of 10^5; this means essentially no S^{2-} is present in aqueous solution. The net dissolution reaction is found by adding the two preceding equations,

$$ZnS(s) + H_2O(\ell) \rightleftharpoons Zn^{2+}(aq) + OH^-(aq) + HS^-(aq)$$

for which the equilibrium constant is

$$[Zn^{2+}][OH^-][HS^-] = K \approx 2 \times 10^{-25}$$

Table 16.3 gives values of the equilibrium constants for comparable reactions of other metal sulfides. As the pH decreases, the concentration of OH^- decreases. At the same time, the concentration of HS^- also decreases as the equilibrium

$$HS^-(aq) + H_3O^+(aq) \rightleftharpoons H_2S(aq) + H_2O(\ell)$$

shifts to the right upon addition of H_3O^+. If both $[OH^-]$ and $[HS^-]$ decrease, then $[Zn^{2+}]$ must increase in order to maintain a constant value for the product of the three concentrations. As a result, the solubility of ZnS(*s*) increases as the pH of the solution decreases. Other metal sulfides behave the same way, becoming more soluble in acidic solution.

A quantitative calculation of metal sulfide solubility requires treating several simultaneous equilibria, as the following example illustrates.

EXAMPLE 16.7

In a solution that is saturated with H_2S, $[H_2S]$ is fixed at 0.1 M. Calculate the molar solubility of FeS(*s*) in such a solution if it is buffered at pH 3.0.

SOLUTION

If the pH is 3.0, then

$$[OH^-] = 1 \times 10^{-11} \text{ M}$$

In addition, the acid ionization of H_2S must be considered:

$$H_2S(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$$

Substitution of $[H_2S] = 0.1$ M for a saturated solution and $[H_3O^+] = 1 \times 10^{-3}$ M (at pH 3.0) into the equilibrium expression for this reaction gives

$$\frac{[H_3O^+][HS^-]}{[H_2S]} = \frac{[1 \times 10^{-3}][HS^-]}{0.1} = K_a = 9.1 \times 10^{-8}$$

$$[HS^-] = 9 \times 10^{-6}\ \text{M}$$

where K_a came from Table 15.2. For the reaction

$$FeS(s) + H_2O(\ell) \rightleftharpoons Fe^{2+}(aq) + HS^-(aq) + OH^-(aq)$$

the equilibrium constant from Table 16.3 is

$$[Fe^{2+}][HS^-][OH^-] = 5 \times 10^{-19}$$

Substituting the values of $[HS^-]$ and $[OH^-]$ and solving for $[Fe^{2+}]$ give

$$[Fe^{2+}](9 \times 10^{-6})(1 \times 10^{-11}) = 5 \times 10^{-19}$$

$$[Fe^{2+}] = 6 \times 10^{-3}\ \text{M}$$

Hence, 6×10^{-3} mol of FeS dissolves per liter under these conditions.

Related Problems: 41, 42

By adjusting the pH through appropriate choice of buffers, as in Example 16.7, conditions can be selected so that metal ions of one element remain entirely in solution, whereas those of a second element in the mixture precipitate almost entirely as solid metal sulfide (Fig. 16.10). Such a procedure is important for separating metal ions in qualitative analysis.


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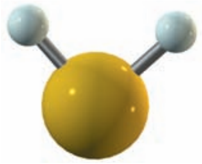
FIGURE 16.10 These sulfides are insoluble at pH 1, so they can be separated out of a mixture containing other, more soluble sulfides. From left to right, they are PbS, Bi_2S_3, CuS, CdS, Sb_2S_3, SnS_2, As_2S_3, and HgS.



Hydrogen sulfide, H_2S, is a poisonous, foul-smelling gas. When dissolved in water, it gives a weak acid, hydrosulfuric acid.

16.6 Complex Ions and Solubility

Many transition-metal ions form **coordination complexes** in solution or in the solid state; these consist of a metal ion surrounded by a group of anions or neutral molecules called **ligands.** The interaction involves the sharing by the metal ion of a lone pair on each ligand molecule, giving a partially covalent bond with that ligand. Such complexes often have strikingly deep colors. When exposed to gaseous ammonia, greenish white crystals of copper sulfate ($CuSO_4$) give a deep blue crystalline solid with the chemical formula $[Cu(NH_3)_4]SO_4$ (Fig. 16.11). The anions in the solid are still sulfate ions (SO_4^{2-}), but the cations are now **complex ions,** or coordination complexes of the central Cu^{2+} ion with four ammonia molecules, $Cu(NH_3)_4^{2+}$. The ammonia molecules coordinate to the copper ion through their lone-pair electrons (Fig. 16.12), acting as Lewis bases toward the metal ion, the Lewis acid. When the solid is dissolved in water, the deep blue color remains. This is evidence that the complex persists in water, because when ordinary $CuSO_4$ (without ammonia ligands) is dissolved in water, a much paler blue color results (see Fig. 16.11b).

Here we explore the effects of the formation of complex ions on equilibria in aqueous solutions. The microscopic structure and bonding in these complexes is presented in Chapter 8.

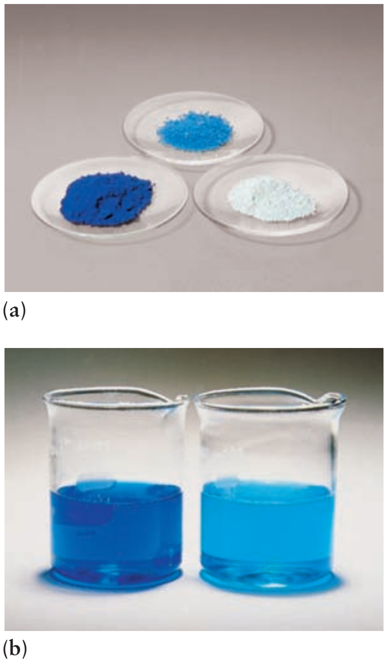


FIGURE 16.11 (a) From left to right, crystals of $Cu(NH_3)_4SO_4$, $CuSO_4 \cdot 5H_2O$, and $CuSO_4$. (b) Aqueous solutions of copper sulfate containing (*left*) and not containing (*right*) ammonia.

(© Thomson Learning/Leon Lewandowski)

Complex-Ion Equilibria

When silver ions are dissolved in an aqueous ammonia solution, doubly coordinated silver–ammonia complexes, shown in Figure 16.13, form in two stepwise reactions:

$$Ag^+(aq) + NH_3(aq) \rightleftarrows Ag(NH_3)^+(aq)$$

$$\frac{[Ag(NH_3)^+]}{[Ag^+][NH_3]} = K_1 = 2.1 \times 10^3$$

$$Ag(NH_3)^+(aq) + NH_3(aq) \rightleftarrows Ag(NH_3)_2^+(aq)$$

$$\frac{[Ag(NH_3)_2^+]}{[Ag(NH_3)^+][NH_3]} = K_2 = 8 \times 10^3$$

If these two chemical equations are added (and their corresponding equilibrium laws are multiplied), the result is

$$Ag^+(aq) + 2\ NH_3(aq) \rightleftarrows Ag(NH_3)_2^+(aq)$$

$$\frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = K_f = K_1K_2 = 1.7 \times 10^7$$

where K_f is the **formation constant** of the full complex ion $Ag(NH_3)_2^+$. Table 16.4 lists formation constants for a representative selection of complex ions. The larger the formation constant K_f, the more stable the corresponding complex ion (for ions with the same number of ligands).

Because K_1 and K_2 of the $Ag(NH_3)_2^+$ complex ion are both large, a silver salt dissolved in water that contains a high concentration of ammonia will be primarily in the form of the complex ion $[Ag(NH_3)_2]^+$ at equilibrium.

TABLE 16.4 Formation Constants of Coordination Complexes in Aqueous Solution

	K_f	K_1	K_2	K_3	K_4	K_5	K_6
Ammines							
$Ag(NH_3)_2^+$	1.7×10^7	2.1×10^3	8.2×10^3				
$Co(NH_3)_6^{2+}$	2.5×10^4	1.0×10^2	32	8.5	4.4	1.1	0.18
$Cu(NH_3)_4^{2+}$	1.1×10^{12}	1.0×10^4	2×10^3	5×10^2	90		
$Ni(NH_3)_6^{2+}$	8×10^{-7}	5×10^2	1.3×10^2	40	12	3.3	0.8
$Zn(NH_3)_4^{2+}$	5×10^8	1.5×10^2	1.8×10^2	2×10^2	90		
Chlorides							
$AgCl_2^-$	1.8×10^5	1.7×10^3	1.0×10^2				
$FeCl_4^-$	0.14	28	4.5	0.1	1.1×10^2		
$HgCl_4^{2-}$	1.2×10^{15}	5.5×10^6	3×10^6	7	10		
$PbCl_4^{2-}$	25	40	1.5	0.8	0.5		
$SnCl_4^{2-}$	30	32	5.4	0.6	0.3		
Hydroxides							
$Co(OH)_3^-$	3×10^{10}	4×10^4	1	8×10^5			
$Cu(OH)_4^{2-}$	3×10^{18}	1×10^7	5×10^6	2×10^3	30		
$Ni(OH)_3^-$	2×10^{11}	9×10^4	4×10^3	6×10^2			
$Pb(OH)_3^-$	4×10^{14}	7×10^7	1.1×10^3	5×10^3			
$Zn(OH)_4^{2-}$	5×10^{14}	2.5×10^4	8×10^6	70	33		

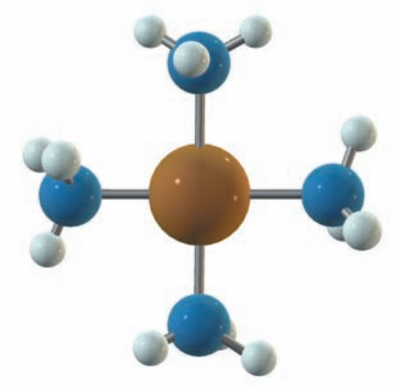


FIGURE 16.12 The structure of $Cu(NH_3)_4^{2+}$.

FIGURE 16.13 The structure of $Ag(NH_3)_2^+$.

EXAMPLE 16.8

Suppose 0.100 mol of $AgNO_3$ is dissolved in 1.00 L of a 1.00 M in solution of NH_3. Calculate the concentrations of the Ag^+ and $Ag(NH_3)^+$ ions present at equilibrium.

SOLUTION

Suppose that most of the Ag^+ is present as $Ag(NH_3)_2^+$ (this will be checked later). Then

$$[Ag(NH_3)_2^+]_0 = 0.100\ \text{M}$$

$$[NH_3]_0 = 1.00\ \text{M} - (2 \times 0.100)\ \text{M} = 0.80\ \text{M}$$

after each silver ion has become complexed with two ammonia molecules. The two stages of the dissociation of the $Ag(NH_3)_2^+$ ion are the reverse reaction of the complexation, so their equilibrium constants are the reciprocals of K_2 and K_1, respectively:

$$Ag(NH_3)_2^+(aq) \rightleftharpoons Ag(NH_3)^+(aq) + NH_3(aq)$$

$$\frac{[Ag(NH_3)^+][NH_3]}{[Ag(NH_3)_2^+]} = \frac{1}{K_2} = \frac{1}{8.2 \times 10^3}$$

$$Ag(NH_3)^+(aq) \rightleftharpoons Ag^+(aq) + NH_3(aq)$$

$$\frac{[Ag^+][NH_3]}{[Ag(NH_3)^+]} = \frac{1}{K_1} = \frac{1}{2.1 \times 10^3}$$

If y mol L^{-1} of $Ag(NH_3)_2^+$ dissociates at equilibrium according to the first equation,

	$Ag(NH_3)_2^+(aq)$	$\rightleftharpoons$ $Ag(NH_3)^+(aq)$	+ $NH_3(aq)$
Initial concentration (M)	0.100	0	0.80
Change in concentration (M)	$-y$	$+y$	$+y$
Equilibrium concentration (M)	$0.100 - y$	y	$0.80 + y$

then the first equilibrium expression becomes

$$\frac{y(0.80 + y)}{0.10 - y} = \frac{1}{K_2} = \frac{1}{8.2 \times 10^3}$$

$$y = 1.5 \times 10^{-5}\ \text{M} = [Ag(NH_3)^+]$$

We can then calculate the concentration of free Ag^+ ions from the equilibrium law for the second step of the dissociation of the complex ion:

$$\frac{[Ag^+][NH_3]}{[Ag(NH_3)^+]} = \frac{1}{K_1}$$

$$\frac{[Ag^+](0.80)}{1.5 \times 10^{-5}} = \frac{1}{2.1 \times 10^3}$$

$$[Ag^+] = 9 \times 10^{-9}\ \text{M}$$

It is clear that the original assumption was correct, and most of the silver present is tied up in the $Ag(NH_3)_2^+$ complex.

Related Problems: 43, 44

There is a close similarity between the working of Example 16.8 and an acid–base calculation. The first step (the assumption that the reaction goes to completion and is followed by a small amount of back dissociation) is analogous to the procedure for dealing with the addition of a small amount of a strong acid to a solution of a weak base. The subsequent calculation of the successive dissociation steps resembles the calculation of polyprotic acid equilibria in Example 15.12. The only difference is that in complex-ion equilibria it is conventional to work with formation constants, which are the inverse of the dissociation constants used in acid–base equilibria.

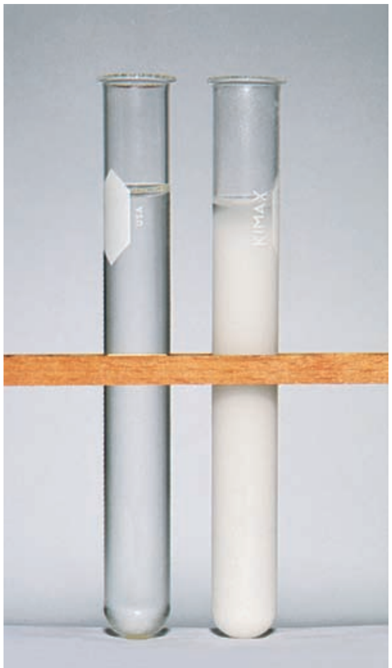


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FIGURE 16.14 An illustration of the effect of complex ion formation on solubility. Each test tube contains 2.0 g AgBr, but the one on the left also contains dissolved thiosulfate ion, which forms a complex ion with Ag^+. Almost none of the white solid AgBr has dissolved in pure water, but all of it has dissolved in the solution containing thiosulfate.

The formation of coordination complexes can have a large effect on the solubility of a compound in water. Silver bromide is only very weakly soluble in water,

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \qquad K_{sp} = 7.7 \times 10^{-13}$$

but addition of thiosulfate ion ($S_2O_3^{2-}$) to the solution allows the complex ion $Ag(S_2O_3)_2^{3-}$ to form:

$$AgBr(s) + 2\ S_2O_3^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq)$$

This greatly increases the solubility of the silver bromide (Fig. 16.14). The formation of this complex ion is an important step in the development of photographic images; thiosulfate ion is a component of the fixer that brings silver bromide into solution from the unexposed portion of the film.

EXAMPLE 16.9

Calculate the solubility of AgBr in a 1.00 M aqueous solution of ammonia.

SOLUTION

We tentatively assume that almost all the silver that dissolves is complexed as $Ag(NH_3)_2^+$ (this will be checked later). The overall reaction is then

$$AgBr(s) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Br^-(aq)$$

Note that this is the sum of the two reactions

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \qquad K_{sp} = 7.7 \times 10^{-13}$$

$$Ag^+(aq) + 2\ NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad K_f = 1.7 \times 10^7$$

so its equilibrium constant is the product $K_{sp}K_f = 1.3 \times 10^{-5}$.

If S mol L^{-1} of AgBr dissolves, then

$$S = [Br^-] \approx [Ag(NH_3)_2^+]$$

$$[NH_3] = 1.00 - 2S$$

because 2 mol of NH_3 is used up for each mole of complex formed. The equilibrium expression is

$$\frac{S^2}{(1.00 - 2S)^2} = K_{sp}K_f = 1.3 \times 10^{-5}$$

$$S = 3.6 \times 10^{-3}\ \text{M} = [Ag(NH_3)_2^+] = [Br^-]$$

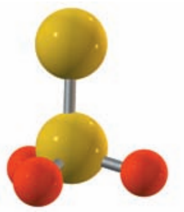
To check the original assumption, calculate the concentration of free silver ion:

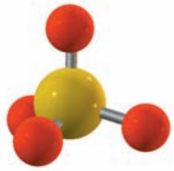
$$[Ag^+] = \frac{K_{sp}}{[Br^-]} = \frac{K_{sp}}{S} = 2.1 \times 10^{-10} \ll [Ag(NH_3)_2^+]$$

verifying that almost all the silver is complexed. The solubility is therefore 3.6×10^{-3} mol L^{-1}, significantly greater than the solubility in pure water:

$$\text{solubility in pure water} = \sqrt{K_{sp}} = 8.8 \times 10^{-7}\ \text{mol L}^{-1}$$

Related Problems: 47, 48





The thiosulfate ion (*top*) is related to the sulfate ion, SO_4^{2-} (*bottom*), by the replacement of one oxygen atom with one sulfur atom. It is prepared, however, by the reaction of elemental sulfur with the sulfite ion (SO_3^{2-}).

Another interesting effect of complex ions on solubilities is illustrated by the addition of iodide ion to a solution containing mercury(II) ion. After a moderate amount of iodide ion has been added, an orange precipitate forms (Fig. 16.15) through the reaction

$$Hg^{2+}(aq) + 2\ I^-(aq) \rightleftharpoons HgI_2(s)$$

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FIGURE 16.15 The "orange tornado" is a striking demonstration of the effects of complex ions on solubility. A solution is prepared with an excess of $I^-(aq)$ over $Hg^{2+}(aq)$ so that the Hg^{2+} is complexed as HgI_3^- and HgI_4^{2-}. A magnetic stirrer is used to create a vortex in the solution. Addition of a solution containing Hg^{2+} down the center of the vortex then causes the orange solid HgI_2 to form in a layer at the edges of the vortex, giving the tornado effect.

With further addition of iodide ion, however, the orange solid redissolves because complex ions form:

$$HgI_2(s) + I^-(aq) \rightleftarrows HgI_3^-(aq)$$

$$HgI_3^-(aq) + I^-(aq) \rightleftarrows HgI_4^{2-}(aq)$$

In the same way, silver chloride will dissolve in a concentrated solution of sodium chloride by forming soluble $AgCl_2^-$ complex ions. Complex ion formation affects solubility in the opposite direction from the common-ion effect of Section 16.3.

Acidity and Amphoterism of Complex Ions

When dissolved in water, many metal ions increase the acidity of the solution. The iron(III) ion is an example: Each dissolved Fe^{3+} ion is strongly solvated by six water molecules, leading to a complex ion $Fe(H_2O)_6^{3+}$. This complex ion can act as a Brønsted–Lowry acid, donating hydrogen ions to the solvent, water:

$$\underset{\text{Acid}_1}{Fe(H_2O)_6^{3+}(aq)} + \underset{\text{Base}_2}{H_2O(\ell)} \rightleftarrows \underset{\text{Acid}_2}{H_3O^+(aq)} + \underset{\text{Base}_1}{Fe(H_2O)_5OH^{2+}(aq)}$$

$$\frac{[H_3O^+][Fe(H_2O)_5OH^{2+}]}{[Fe(H_2O)_6^{3+}]} = K_a = 7.7 \times 10^{-3}$$

Metal ion hydrolysis fits into the general scheme of the Brønsted–Lowry acid–base reaction.

EXAMPLE 16.10

Calculate the pH of a solution that is 0.100 M in $Fe(NO_3)_3$.

SOLUTION

The iron(III) is present as $Fe(H_2O)_6^{3+}$, which reacts as a weak acid:

$$Fe(H_2O)_6^{3+}(aq) + H_2O(\ell) \rightleftarrows Fe(H_2O)_5OH^{2+}(aq) + H_3O^+(aq)$$

with K_a equal to 7.7×10^{-3}. If y mol L^{-1} of $[Fe(H_2O)_6]^{3+}$ reacts, then (neglecting the ionization of water itself)

$$[H_3O^+] = [Fe(H_2O)_5OH^{2+}] = y$$

$$[Fe(H_2O)_6^{3+}] = 0.100 - y$$

The equilibrium expression has the form

$$\frac{y^2}{0.100 - y} = 7.7 \times 10^{-3}$$

$$y = 2.4 \times 10^{-2}\ \text{M} = [H_3O^+]$$

so the pH is 1.62. Solutions of iron(III) salts are strongly acidic.

Related Problems: 51, 52

Another acceptable way to write the reaction that makes iron(III) solutions acidic is

$$Fe^{3+}(aq) + 2\,H_2O(\ell) \rightleftarrows H_3O^+(aq) + FeOH^{2+}(aq)$$

in which the specific mention of the six waters of hydration is now omitted. The $FeOH^{2+}$ complex ions are brown, but Fe^{3+} ions are almost colorless. This reaction occurs to a sufficient extent to make a solution of $Fe(NO_3)_3$ in water pale brown. When strong acid is added, the equilibrium is driven back to the left and the color fades. Table 16.5 gives values of the pH for 0.1 M solutions of several metal ions. Those that form strong complexes with hydroxide ion have low pH

TABLE 16.5 pH of 0.1 M Aqueous Metal Nitrate Solutions at 25°C

Metal Nitrate	PH
$Fe(NO_3)_3$	1.6
$Pb(NO_3)_2$	3.6
$Cu(NO_3)_2$	4.0
$Zn(NO_3)_2$	5.3
$Ca(NO_3)_2$	6.7
$NaNO_3$	7.0

(Fig. 16.16), whereas those that do not form such complexes give neutral solutions (pH 7).

Different cations behave differently as water ligands are replaced by hydroxide ions in an increasingly basic solution. A particularly interesting example is Zn^{2+}. It forms a series of hydroxo complex ions:

$$Zn^{2+}(aq) + OH^-(aq) \rightleftarrows ZnOH^+(aq)$$

$$ZnOH^+(aq) + OH^-(aq) \rightleftarrows Zn(OH)_2(s)$$

$$Zn(OH)_2(s) + OH^-(aq) \rightleftarrows Zn(OH)_3^-(aq)$$

$$Zn(OH)_3^-(aq) + OH^-(aq) \rightleftarrows Zn(OH)_4^{2-}(aq)$$

In the Brønsted–Lowry theory, a polyprotic acid, $Zn(H_2O)_4^{2+}(aq)$, donates hydrogen ions in succession to make all the product ions. The second product, $Zn(OH)_2$, is amphoteric; it can react as either acid or base. It is only slightly soluble in pure water (its K_{sp} is only 1.9×10^{-17}). If enough acid is added to solid $Zn(OH)_2$, the OH^- ligands are removed, forming the soluble Zn^{2+} ion; if enough base is added, OH^- ligands attach to form the soluble $Zn(OH)_4^{2+}$ (zincate) ion. Thus, $Zn(OH)_2$ is soluble in strongly acidic *or* strongly basic solutions but is only slightly soluble at intermediate pH values (Fig. 16.17). This amphoterism can be used to separate Zn^{2+} from other cations that do not share the property. For example, Mg^{2+} adds a maximum of two OH^- ions to form $Mg(OH)_2$, a sparingly soluble hydroxide. Further addition of OH^- does not lead to the formation of new complex ions. If a mixture of Mg^{2+} and Zn^{2+} ions is made sufficiently basic, the Mg^{2+} precipitates as $Mg(OH)_2$ but the zinc remains in solution as $Zn(OH)_4^{2-}$, allowing the two to be separated. In the same way, aluminum is separated from iron industrially by dissolving solid $Al(OH)_3$ in strong base as $Al(OH)_4^-(aq)$ while $Fe(OH)_3$ remains as a precipitate.


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FIGURE 16.16 The acidity of metal ions is illustrated by the vigorous reaction of anhydrous $AlCl_3$ with water to generate hydrated aluminum oxides, HCl(*aq*), and heat. The HCl turns the indicator to its red acid form.


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FIGURE 16.17 Zinc hydroxide is insoluble in water (*center*) but dissolves readily in acid (*left*) and base (*right*). The indicator used is bromocresol red, which turns from red to yellow in acidic solution.

CHAPTER SUMMARY

Dissolution–precipitation reactions involve equilibrium between a substance in its solid form and molecules or ions of that same substance dissolved in solution. This equilibrium is described by the mass action law, so knowledge of the equilibrium constant permits manipulation of the concentrations in solution through the principles described in Chapter 14. Numerous separation and purification procedures are based on such manipulations. The significance of these dissolution–precipitation equilibria in practical applications is comparable to that of acid–base reactions. Solutions of slightly soluble solids are said to be saturated when the dissolved concentration is at equilibrium with the solid. In accordance with the principle of Le Châtelier, if the solution goes to a state of supersaturation, it will return to equilibrium by precipitating solid out of solution. Similarly, according to Le Châtelier, solubility can be controlled by increasing temperature (for endothermic reactions) or decreasing temperature (for exothermic reactions). Solubility is greatly influenced by the presence of other species to the solution, through the way they shift the equilibrium concentration of the dissolved solid species. This general principle explains the common ion effect and the influence of pH on solubility.

CUMULATIVE EXERCISE

Carbonate Minerals

The carbonates are among the most abundant and important minerals in the earth's crust. When these minerals come into contact with fresh water or seawater, solubility equilibria are established that greatly affect the chemistry of the natural waters. Calcium carbonate ($CaCO_3$), the most important natural carbonate, makes up limestone and other forms of rock such as marble. Other carbonate minerals include dolomite, $CaMg(CO_3)_2$, and magnesite, $MgCO_3$. These compounds are sufficiently soluble that their solutions are nonideal, so calculations based on solubility product expressions are only approximate.

(a) The rare mineral nesquehonite contains $MgCO_3$ together with water of hydration. A sample containing 21.7 g of nesquehonite is acidified and heated, and the volume of $CO_2(g)$ produced is measured to be 3.51 L at 0°C and $P = 1$ atm. Assuming all the carbonate has reacted to form CO_2, give the chemical formula for nesquehonite.

(b) Write a chemical equation and a solubility product expression for the dissolution of dolomite in water.

(c) In a sufficiently basic solution, the carbonate ion does not react significantly with water to form hydrogen carbonate ion. Calculate the solubility (in grams per liter) of limestone (calcium carbonate) in a 0.10 M solution of sodium hydroxide. Use the K_{sp} from Table 16.2.

(d) In a strongly basic 0.10 M solution of Na_2CO_3, the concentration of CO_3^{2-} is 0.10 M. What is the gram solubility of limestone in this solution? Compare your answer with that for part (c).

(e) In a mountain lake having a pH of 8.1, the total concentration of carbonate species, $[CO_3^{2-}] + [HCO_3^-]$, is measured to be 9.6×10^{-4} M, whereas the concentration of Ca^{2+} is 3.8×10^{-4} M. Calculate the concentration of CO_3^{2-} in this lake, using $K_a = 4.8 \times 10^{-11}$ for the acid ionization of HCO_3^- to CO_3^{2-}. Is the lake unsaturated, saturated, or supersaturated with respect to $CaCO_3$?

(f) Will acid rainfall into the lake increase or decrease the solubility of limestone rocks in the lake's bed?

(g) Seawater contains a high concentration of Cl^- ions, which form weak complexes with calcium, such as the ion pair $CaCl^+$. Does the presence of such complexes increase or decrease the equilibrium solubility of $CaCO_3$ in seawater?

Answers

(a) $MgCO_3 \cdot 3H_2O$

(b) $CaMg(CO_3)_2(s) \rightleftharpoons Ca^{2+}(aq) + Mg^{2+}(aq) + 2\ CO_3^{2-}(aq)$

$$[Ca^{2+}][Mg^{2+}][CO_3^{2-}]^2 = K_{sp}$$

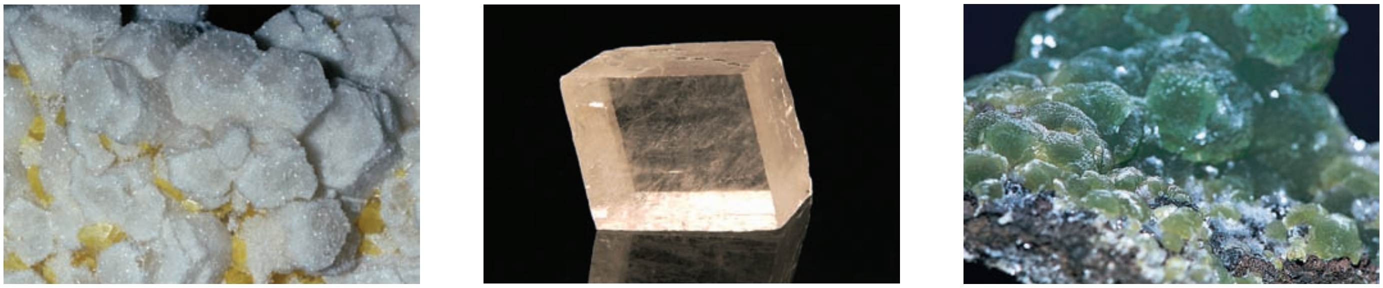
(c) 9.3×10^{-3} g L^{-1}

(d) 8.7×10^{-6} g L^{-1}, smaller than in part (c) because of the common-ion effect

(e) 5.8×10^{-6} M. $Q = 2.2 \times 10^{-9} < K_{sp} = 8.7 \times 10^{-9}$, so the lake is slightly less than saturated

(f) Increase

(g) Increase



Carbonate minerals. Calcite (*left*) and aragonite (*middle*) are both $CaCO_3$, and smithsonite (*right*) is $ZnCO_3$.

(Left, © Thomson Learning/Charles D. Winters; middle, Ken Lucas/Visuals Unlimited; right, copyright Tom McHugh/Photo Researchers, Inc.)

CHAPTER REVIEW

The Nature of Solubility Equilibria

- A substance in its solid state may be in contact with a solution in which this same substance is dissolved. Molecules of this substance pass back and forth between the solid state and the dissolved state.
- When there is equilibrium between the solid substance and its dissolved form, the solution is *saturated* and cannot accommodate more solute. A nonequilibrium state can exist in which there is temporarily more dissolved solute than the equilibrium concentration. This state is called supersaturated.
- The solubility of a substance is the greatest amount that will dissolve in a specified volume of solvent at a specified temperature. Solubility is expressed in g L^{-1} or mol L^{-1}.
- Solubility is temperature dependent. By Le Châtelier's principle it can either increase or decrease with increasing temperature depending on whether the dissolution reaction is endothermic or exothermic.

Ionic Equilibria between Solids and Solutions

- Slightly soluble ionic solids dissociate in solution, so the solid is in equilibrium with its dissolved cations and anions.
- $AB(s) \rightleftharpoons A^+(aq) + B^-(aq)$
  $K_{sp} = [A^+]\,[B^-] = S^2$ if S is the molar solubility.
- $AB_2(s) \rightleftharpoons A^+(aq) + 2\,B^-(aq)$
  $K_{sp} = [A^+]\,[B^-]^2 = 4S^3$, and so on, for different stoichiometric ratios.

Precipitation and the Solubility Product

- $Q = [A^+]\,[B^-]$ at any point in the reaction. If $Q > K_{sp}$ a precipitate will form.
- The common ion effect—no matter what the sources of the ions, the product of their concentrations cannot exceed K_{sp} under equilibrium conditions.

Special Chemical Effects in Solubility

- Solubility of metal hydroxides increases at lower pH because the acid present ties up hydroxide ions in solution and so shifts the dissolution equilibrium to the right.
- Solubility of salts in which the anion is a weak base increases at lower pH because the hydronium ion in solution consumes the anion and so shifts the dissolution equilibrium to the right.
- Solubility of metal ions can be increased by forming coordination complexes with ligands.
- Metal ions undergo hydrolysis reactions in water by forming hydrated complex ions that increase the acidity of the solution.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Discuss the dynamical processes that lead to solubility equilibria (Section 16.1).
2. Relate the solubilities of sparingly soluble salts in water to their solubility product constants (Section 16.2, Problems 7–16).
3. Use the reaction quotient to predict whether a precipitate will form when two solutions are mixed, and then calculate the equilibrium concentrations that result (Section 16.3, Problems 17–24).

4. Calculate the solubility of a sparingly soluble salt in a solution that contains a given concentration of a common ion (Section 16.3, Problems 25–30).
5. Determine the dependence on pH of the solubility of a salt of a weak base (Section 16.4, Problems 33–34).
6. Specify the optimal conditions for the separation of two elements on the basis of the differing solubilities of their ionic compounds (Section 16.5, Problems 35–42).
7. Calculate the concentrations of molecular and ionic species in equilibrium with complex ions (Section 16.6, Problems 43–46).
8. Determine the effect of complex-ion formation on the solubility of sparingly soluble salts involving a common cation (Section 16.6, Problems 47–48).
9. Calculate the pH of aqueous solutions containing metal cations (Section 16.6, Problems 49–54).

PROBLEMS

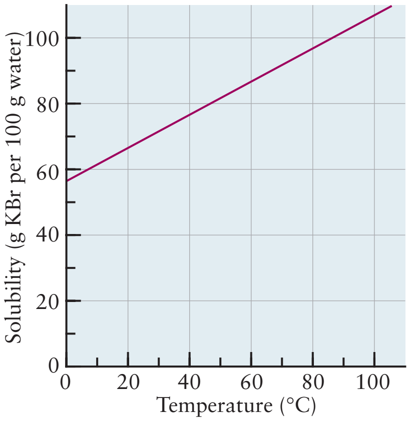
Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

The Nature of Solubility Equilibria

1. Gypsum has the formula $CaSO_4{\cdot}2H_2O$. Plaster of Paris has the chemical formula $CaSO_4{\cdot}\frac{1}{2}\ H_2O$. In making wall plaster, water is added to plaster of Paris and the mixture then hardens into solid gypsum. How much water (in liters, at a density of 1.00 kg L^{-1}) should be added to 25.0 kg of plaster of Paris to turn it into gypsum, assuming no loss from evaporation?

2. A 1.00-g sample of magnesium sulfate is dissolved in water, and the water is then evaporated away until the residue is bone dry. If the temperature of the water is kept between 48°C and 69°C, the solid that remains weighs 1.898 g. If the experiment is repeated with the temperature held between 69°C and 100°C, however, the solid has a mass of 1.150 g. Determine how many waters of crystallization per $MgSO_4$ there are in each of these two solids.

3. The following graph shows the solubility of KBr in water in units of grams of KBr per 100 g of H_2O. If 80 g of KBr is added to 100 g of water at 10°C and the mixture is heated slowly, at what temperature will the last KBr dissolve?



4. Figure 16.3 shows the solubility of $AgNO_3$ in water in units of moles of $AgNO_3$ per kilogram of H_2O. If 255 g of $AgNO_3$ is added to 100 g of water at 95°C and cooled slowly, at what temperature will the solution become saturated?

Ionic Equilibria between Solids and Solutions

5. Iron(III) sulfate, $Fe_2(SO_4)_3$, is a yellow compound that is used as a coagulant in water treatment. Write a balanced chemical equation and a solubility product expression for its dissolution in water.

6. Lead antimonate, $Pb_3(SbO_4)_2$, is used as an orange pigment in oil-based paints and in glazes. Write a balanced chemical equation and a solubility product expression for its dissolution in water.

7. Thallium(I) iodate ($TlIO_3$) is only slightly soluble in water. Its K_{sp} at 25°C is 3.07×10^{-6}. Estimate the solubility of thallium(I) iodate in water in units of grams per 100.0 mL of water.

8. Thallium thiocyanate (TlSCN) is only slightly soluble in water. Its K_{sp} at 25°C is 1.82×10^{-4}. Estimate the solubility of thallium thiocyanate in units of grams per 100.0 mL of water.

9. Potassium perchlorate, $KClO_4$, has a K_{sp} at 25°C of 1.07×10^{-2}. Compute its solubility in grams per liter of solution.

10. Ammonium hexachloroplatinate(IV), $(NH_4)_2(PtCl_6)$, is one of the few sparingly soluble ammonium salts. Its K_{sp} at 20°C is 5.6×10^{-6}. Compute its solubility in grams per liter of solution.

11. The solubility product constant of mercury(I) iodide is 1.2×10^{-28} at 25°C. Estimate the concentration of Hg_2^{2+} and I^- in equilibrium with solid Hg_2I_2.

12. The solubility product constant of Hg_2Cl_2 is 2×10^{-18} at 25°C. Estimate the concentration of Hg_2^{2+} and Cl^- in equilibrium with solid Hg_2Cl_2 at 25°C.

13. The solubility of silver chromate (Ag_2CrO_4) in 500 mL of water at 25°C is 0.0129 g. Calculate its solubility product constant.

14. At 25°C, 400 mL of water can dissolve 0.00896 g of lead iodate, $Pb(IO_3)_2$. Calculate K_{sp} for lead iodate.

15. At 100°C, water dissolves 1.8×10^{-2} g of AgCl per liter. Compute the K_{sp} of AgCl at this temperature.

16. A mass of 0.017 g of silver dichromate ($Ag_2Cr_2O_7$) will dissolve in 300 mL of water at 25°C. Calculate the solubility product constant K_{sp} of silver dichromate.

Precipitation and the Solubility Product

17. A solution of barium chromate ($BaCrO_4$) is prepared by dissolving 6.3×10^{-3} g of this yellow solid in 1.00 L of hot water. Will solid barium chromate precipitate upon cooling to 25°C, according to the solubility product expression? Explain.

18. A solution is prepared by dissolving 0.090 g of PbI_2 in 1.00 L of hot water and cooling the solution to 25°C. Will solid precipitate result from this process, according to the solubility product expression? Explain.

19. A solution is prepared by mixing 250.0 mL of 2.0×10^{-3} M $Ce(NO_3)_3$ and 150.0 mL of 10×10^{-2} M KIO_3 at 25°C. Determine whether $Ce(IO_3)_3(s)$ ($K_{sp} = 1.9 \times 10^{-10}$) tends to precipitate from this mixture.

20. Suppose 100.0 mL of a 0.0010 M $CaCl_2$ solution is added to 50.0 mL of a 6.0×10^{-5} M NaF solution at 25°C. Determine whether $CaF_2(s)$ ($K_{sp} = 3.9 \times 10^{-11}$) tends to precipitate from this mixture.

21. Suppose 50.0 mL of a 0.0500 M solution of $Pb(NO_3)_2$ is mixed with 40.0 mL of a 0.200 M solution of $NaIO_3$ at 25°C. Calculate the $[Pb^{2+}]$ and $[IO_3^-]$ when the mixture comes to equilibrium. At this temperature, K_{sp} for $Pb(IO_3)_2$ is 2.6×10^{-13}.

22. Silver iodide (AgI) is used in place of silver chloride for the fastest photographic film because it is more sensitive to light and can therefore form an image in a very short exposure time. A silver iodide emulsion is prepared by adding 6.60 L of 0.10 M NaI solution to 1.50 L of 0.080 M $AgNO_3$ solution at 25°C. Calculate the concentration of silver ion remaining in solution when the mixture comes to equilibrium and its chemical amount relative to the amount present initially.

23. When 50.0 mL of 0.100 M $AgNO_3$ and 30.0 mL of 0.0600 M Na_2CrO_4 are mixed, a precipitate of silver chromate (Ag_2CrO_4) is formed. The solubility product K_{sp} of silver chromate in water at 25°C is 1.9×10^{-12}. Calculate the $[Ag^+]$ and $[CrO_4^{2-}]$ remaining in solution at equilibrium.

24. When 40.0 mL of 0.0800 M $Sr(NO_3)_2$ and 80.0 mL of 0.0500 M KF are mixed, a precipitate of strontium fluoride (SrF_2) is formed. The solubility product K_{sp} of strontium fluoride in water at 25°C is 2.8×10^{-9}. Calculate the $[Sr^{2+}]$ and $[F^-]$ remaining in solution at equilibrium.

25. Calculate the solubility (in mol L^{-1}) of $CaF_2(s)$ at 25°C in a 0.040 M aqueous solution of NaF.

26. Calculate the mass of AgCl that can dissolve in 100 mL of 0.150 M NaCl solution.

27. The solubility product of nickel(II) hydroxide, $Ni(OH)_2$, at 25°C is $K_{sp} = 1.6 \times 10^{-16}$.

(a) Calculate the molar solubility of $Ni(OH)_2$ in pure water at 25°C.

(b) Calculate the molar solubility of $Ni(OH)_2$ in 0.100 M NaOH.

28. Silver arsenate (Ag_3AsO_4) is a slightly soluble salt having a solubility product of $K_{sp} = 1.0 \times 10^{-22}$ at 25°C for the equilibrium

$$Ag_3AsO_4(s) \rightleftharpoons 3\,Ag^+(aq) + AsO_4^{3-}(aq)$$

(a) Calculate the molar solubility of silver arsenate in pure water at 25°C.

(b) Calculate the molar solubility of silver arsenate in 0.10 M $AgNO_3$.

29. A saturated solution of $Mg(OH)_2$ at 25°C is prepared by equilibrating solid $Mg(OH)_2$ with water. Concentrated NaOH is then added until the solubility of $Mg(OH)_2$ is 0.0010 times that in H_2O alone. (Ignore the change in volume resulting from the addition of NaOH.) The solubility product K_{sp} of $Mg(OH)_2$ is 1.2×10^{-11} at 25°C. Calculate the concentration of hydroxide ion in the solution after the addition of the NaOH.

30. A saturated solution of BaF_2 at 25°C is prepared by equilibrating solid BaF_2 with water. Powdered NaF is then dissolved in the solution until the solubility of BaF_2 is 1.0% of that in H_2O alone. The solubility product K_{sp} of BaF_2 is 1.7×10^{-6} at 25°C. Calculate the concentration of fluoride ion in the solution after addition of the powdered NaF.

The Effects of pH on Solubility

31. Compare the molar solubility of AgOH in pure water with that in a solution buffered at pH 7.00. Note the difference between the two: When AgOH is dissolved in pure water, the pH does not remain at 7.

32. Compare the molar solubility of $Mg(OH)_2$ in pure water with that in a solution buffered at pH 9.00.

33. For each of the following ionic compounds, state whether the solubility will increase, decrease, or remain unchanged as a solution at pH 7 is made acidic.

(a) PbI_2 (b) AgOH (c) $Ca_3(PO_4)_2$

34. For each of the following ionic compounds, state whether the solubility will increase, decrease, or remain unchanged as a solution at pH 7 is made acidic.

(a) $SrCO_3$ (b) Hg_2Br_2 (c) MnS

A DEEPER LOOK . . . Selective Precipitation of Ions

35. An aqueous solution at 25°C is 0.10 M in both Mg^{2+} and Pb^{2+} ions. We wish to separate the two kinds of metal ions by taking advantage of the different solubilities of their oxalates, MgC_2O_4 and PbC_2O_4.

(a) What is the highest possible oxalate ion concentration that allows only one solid oxalate salt to be present at equilibrium? Which ion is present in the solid—Mg^{2+} or Pb^{2+}?

(b) What fraction of the less soluble ion still remains in solution under the conditions of part (a)?

36. An aqueous solution at 25°C is 0.10 M in Ba^{2+} and 0.50 M in Ca^{2+} ions. We wish to separate the two by taking advantage of the different solubilities of their fluorides, BaF_2 and CaF_2.

(a) What is the highest possible fluoride ion concentration that allows only one solid fluoride salt to be present at equilibrium? Which ion is present in the solid—Ba^{2+} or Ca^{2+}?

(b) What fraction of the less soluble ion still remains in solution under the conditions of part (a)?

37. The cations in an aqueous solution that contains 0.100 M $Hg_2(NO_3)_2$ and 0.0500 M $Pb(NO_3)_2$ are to be separated by taking advantage of the difference in the solubilities of their iodides. $K_{sp}(PbI_2) = 1.4 \times 10^{-8}$ and $K_{sp}(Hg_2I_2) = 1.2 \times 10^{-28}$. What should be the concentration of iodide ion for the best separation? In the "best" separation, one of the cations should remain entirely in solution and the other should precipitate as fully as possible.

38. The cations in an aqueous solution that contains 0.150 M $Ba(NO_3)_2$ and 0.0800 M $Ca(NO_3)_2$ are to be separated by taking advantage of the difference in the solubilities of their sulfates. $K_{sp}(BaSO_4) = 1.1 \times 10^{-10}$ and $K_{sp}(CaSO_4) = 2.4 \times 10^{-5}$. What should be the concentration of sulfate ion for the best separation?

39. Calculate the $[Zn^{2+}]$ in a solution that is in equilibrium with $ZnS(s)$ and in which $[H_3O^+] = 1.0 \times 10^{-5}$ M and $[H_2S] = 0.10$ M.

40. Calculate the $[Cd^{2+}]$ in a solution that is in equilibrium with $CdS(s)$ and in which $[H_3O^+] = 1.0 \times 10^{-3}$ M and $[H_2S] = 0.10$ M.

41. What is the highest pH at which 0.10 M Fe^{2+} will remain entirely in a solution that is saturated with H_2S at a concentration of $[H_2S] = 0.10$ M? At this pH, what would be the concentration of Pb^{2+} in equilibrium with solid PbS in this solution?

42. What is the highest pH at which 0.050 M Mn^{2+} will remain entirely in a solution that is saturated with H_2S at a concentration of $[H_2S] = 0.10$ M? At this pH, what would be the concentration of Cd^{2+} in equilibrium with solid CdS in this solution?

Complex Ions and Solubility

43. Suppose 0.10 mol of $Cu(NO_3)_2$ and 1.50 mol of NH_3 are dissolved in water and diluted to a total volume of 1.00 L. Calculate the concentrations of $Cu(NH_3)_4^{2+}$ and of Cu^{2+} at equilibrium.

44. The formation constant of the $TlCl_4^-$ complex ion is 1×10^{18}. Suppose 0.15 mol of $Tl(NO_3)_3$ is dissolved in 1.00 L of a 0.50 M solution of NaCl. Calculate the concentration at equilibrium of $TlCl_4^-$ and of Tl^{3+}.

45. The organic compound "18-crown-6" binds alkali metals in aqueous solution by wrapping around and enfolding the ion. It presents a niche that nicely accommodates the K^+ ion but is too small for the Rb^+ ion and too large for the Na^+ ion. The values of the equilibrium constants show this:

$$Na^+(aq) + \text{18-crown-6}(aq) \rightleftharpoons \text{Na-crown}^+(aq) \qquad K = 6.6$$

$$K^+(aq) + \text{18-crown-6}(aq) \rightleftharpoons \text{K-crown}^+(aq) \qquad K = 111.6$$

$$Rb^+(aq) + \text{18-crown-6}(aq) \rightleftharpoons \text{Rb-crown}^+(aq) \qquad K = 36$$

An aqueous solution is initially 0.0080 M in 18-crown-6(*aq*) and also 0.0080 M in $K^+(aq)$. Compute the equilibrium concentration of free K^+. ("Free" means not tied up with the 18-crown-6.) Compute the concentration of free Na^+ if the solution contains 0.0080 M $Na^+(aq)$ instead of $K^+(aq)$.

46. The organic compound 18-crown-6 (see preceding problem) also binds strongly with the alkali metal ions in methanol.

$$K^+ + \text{18-crown-6} \rightleftharpoons [\text{complex}]^+$$

In methanol solution the equilibrium constant is 1.41×10^6. A similar reaction with Cs^+ has an equilibrium constant of only 2.75×10^4. A solution is made (in methanol) containing 0.020 mol L^{-1} each of K^+ and Cs^+. It also contains 0.30 mol L^{-1} of 18-crown-6. Compute the equilibrium concentrations of both the uncomplexed K^+ and the uncomplexed Cs^+.

47. Will silver chloride dissolve to a significantly greater extent in a 1.00 M NaCl solution than in pure water due to the possible formation of $AgCl_2^-$ ions? Use data from Tables 16.2 and 16.4 to provide a quantitative answer to this question. What will happen in a 0.100 M NaCl solution?

48. Calculate how many grams of silver chloride will dissolve in 1.0 L of a 1.0 M NH_3 solution through formation of the complex ion $Ag(NH_3)_2^+$.

49. The pH of a 0.2 M solution of $CuSO_4$ is 4.0. Write chemical equations to explain why a solution of this salt is neither basic [from the reaction of $SO_4^{2-}(aq)$ with water] nor neutral, but acidic.

50. Will a 0.05 M solution of $FeCl_3$ be acidic, basic, or neutral? Explain your answer by writing chemical equations to describe any reactions taking place.

51. The acid ionization constant for $Co(H_2O)_6^{2+}(aq)$ is 3×10^{-10}. Calculate the pH of a 0.10 M solution of $Co(NO_3)_2$.

52. The acid ionization constant for $Fe(H_2O)_6^{2+}(aq)$ is 3×10^{-6}. Calculate the pH of a 0.10 M solution of $Fe(NO_3)_2$, and compare it with the pH of the corresponding iron(III) nitrate solution from Example 16.10.

53. A 0.15 M aqueous solution of the chloride salt of the complex ion $Pt(NH_3)_4^{2+}$ is found to be weakly acidic with a pH of 4.92. This is initially puzzling because the Cl^- ion in water is not acidic and NH_3 in water is *basic,* not acidic. Finally, it is suggested that the $Pt(NH_3)_4^{2+}$ ion as a group donates hydrogen ions. Compute the K_a of this acid, assuming that just one hydrogen ion is donated.

54. The pH of a 0.10 M solution of $Ni(NO_3)_2$ is 5.0. Calculate the acid ionization constant of $Ni(H_2O)_6^{2+}(aq)$.

* **55.** K_{sp} for $Pb(OH)_2$ is 4.2×10^{-15}, and K_f for $Pb(OH)_3^-$ is 4×10^{14}. Suppose a solution whose initial concentration of $Pb^{2+}(aq)$ is 1.00 M is brought to pH 13.0 by addition of solid NaOH. Will solid $Pb(OH)_2$ precipitate, or will the lead be dissolved as $Pb(OH)_3^-(aq)$? What will be $[Pb^{2+}]$ and $[Pb(OH)_3^-]$ at equilibrium? Repeat the calculation for an initial Pb^{2+} concentration of 0.050 M. (*Hint:* One way to solve this problem is to *assume* that $Pb(OH)_2(s)$ is present and calculate $[Pb^{2+}]$ and $[Pb(OH)_3^-]$ that would be in equilibrium with the solid. If the sum of these is less than the original $[Pb^{2+}]$, the remainder can be assumed to have precipitated. If not, there is a contradiction and we must assume that *no* $Pb(OH)_2(s)$ is present. In this case we can calculate $[Pb^{2+}]$ and $[Pb(OH)_3^-]$ directly from K_f.)

* **56.** K_{sp} from $Zn(OH)_2$ is 4.5×10^{-17}, and K_f for $Zn(OH)_4^{2-}$ is 5×10^{14}. Suppose a solution whose initial concentration of $Zn^{2+}(aq)$ is 0.010 M is brought to pH 14.0 by addition of solid NaOH. Will solid $Zn(OH)_2$ precipitate, or will the zinc be dissolved as $Zn(OH)_4^{2-}(aq)$? What will be $[Zn^{2+}]$ and $[Zn(OH)_4^{2-}]$ at equilibrium? Repeat the calculation at pH 13 for an initial Zn^{2+} concentration of 0.10 M. See the hint in problem 55.

ADDITIONAL PROBLEMS

57. Write a chemical equation for the dissolution of mercury(I) chloride in water, and give its solubility product expression.

* 58. Magnesium ammonium phosphate has the formula $MgNH_4PO_4 \cdot 6H_2O$. It is only slightly soluble in water (its K_{sp} is 2.3×10^{-13}). Write a chemical equation and the corresponding equilibrium law for the dissolution of this compound in water.

59. Soluble barium compounds are poisonous, but barium sulfate is routinely ingested as a suspended solid in a "barium cocktail" to improve the contrast in x-ray images. Calculate the concentration of dissolved barium per liter of water in equilibrium with solid barium sulfate.

60. A saturated aqueous solution of silver perchlorate ($AgClO_4$) contains 84.8% by mass $AgClO_4$, but a saturated solution of $AgClO_4$ in 60% aqueous perchloric acid contains only 5.63% by mass $AgClO_4$. Explain this large difference using chemical equations.

61. Suppose 140 mL of 0.0010 M $Sr(NO_3)_2$ is mixed with enough 0.0050 M NaF to make 1.00 L of solution. Will $SrF_2(s)$ ($K_{sp} = 2.8 \times 10^{-9}$) precipitate at equilibrium? Explain.

62. The concentration of calcium ion in a town's supply of drinking water is 0.0020 M. (This water is referred to as hard water because it contains such a large concentration of Ca^{2+}.) Suppose the water is to be fluoridated by the addition of NaF for the purpose of reducing tooth decay. What is the maximum concentration of fluoride ion that can be achieved in the water before precipitation of CaF_2 begins? Will the water supply attain the level of fluoride ion recommended by the U.S. Public Health Service, about 5×10^{-5} M (1 mg fluorine per liter)?

63. Suppose that 150 mL of 0.200 M K_2CO_3 and 100 mL of 0.400 M $Ca(NO_3)_2$ are mixed together. Assume that the volumes are additive, that $CaCO_3$ is completely insoluble, and that all other substances that might be formed are soluble. Calculate the mass of $CaCO_3$ precipitated, and calculate the concentrations in the final solution of the four ions that were present initially.

64. The solubility of $CaCO_3$ in water is about 7 mg L^{-1}. Show how one can calculate the solubility product of $BaCO_3$ from this information and from the fact that when sodium carbonate solution is added slowly to a solution containing equimolar concentrations of Ca^{2+} and Ba^{2+}, no $CaCO_3$ is formed until about 90% of the Ba^{2+} has been precipitated as $BaCO_3$.

65. It is sometimes asserted that carbonates are soluble in strong acids because a gas is formed that escapes (CO_2). Suppose that CO_2 were extremely soluble in water (as, for example, ammonia is) and therefore it did not leave the site of the reaction, but that otherwise, its chemistry was unchanged. Would calcium carbonate be soluble in strong acids? Explain.

66. The solubility products of $Fe(OH)_3$ and $Ni(OH)_2$ are about 10^{-36} and 6×10^{-18}, respectively. Find the approximate pH range suitable for the separation of Fe^{3+} and Ni^{2+} by precipitation of $Fe(OH)_3$ from a solution initially 0.01 M in each ion, as follows: (a) Calculate the lowest pH at which all but 0.1% of the Fe^{3+} will be precipitated as $Fe(OH)_3$; (b) calculate the highest pH possible without precipitation of $Ni(OH)_2$.

67. The two solids $CuBr(s)$ and $AgBr(s)$ are only very slightly soluble in water: $K_{sp}(CuBr) = 4.2 \times 10^{-8}$ and $K_{sp}(AgBr) = 7.7 \times 10^{-13}$. Some $CuBr(s)$ and $AgBr(s)$ are both mixed into a quantity of water that is then stirred until it is saturated with respect to both solutes. Next, a small amount of KBr is added and dissolves completely. Compute the ratio of $[Cu^+]$ to $[Ag^+]$ after the system reestablishes equilibrium.

* 68. The two salts $BaCl_2$ and Ag_2SO_4 are both far more soluble in water than either $BaSO_4$ ($K_{sp} = 1.1 \times 10^{-10}$) or AgCl ($K_{sp} = 1.6 \times 10^{-10}$) at 25°C. Suppose 50.0 mL of 0.040 M $BaCl_2(aq)$ is added to 50.0 mL of 0.020 M $Ag_2SO_4(aq)$. Calculate the concentrations of SO_4^{2-} (*aq*), Cl^- (*aq*), $Ba^{2+}(aq)$, and $Ag^+(aq)$ that remain in solution at equilibrium.

69. The Mohr method is a technique for determining the amount of chloride ion in an unknown sample. It is based on the difference in solubility between silver chloride (AgCl; $K_{sp} = 1.6 \times 10^{-10}$) and silver chromate ($Ag_2CrO_4$; $K_{sp} = 1.9 \times 10^{-12}$). In using this method, one adds a small amount of chromate ion to a solution with unknown chloride concentration. By measuring the volume of $AgNO_3$ added before the appearance of the red silver chromate, one can determine the amount of Cl^- originally present. Suppose we have a solution that is 0.100 M in Cl^- and 0.00250 M in CrO_4^{2-}. If we add 0.100 M $AgNO_3$ solution drop by drop, will AgCl or Ag_2CrO_4 precipitate first? When $Ag_2CrO_4(s)$ first appears, what fraction of the Cl^- originally present remains in solution?

70. Oxide ion, like sulfide ion, is a strong base. Write an equation for the dissolution of CaO in water and give its equilibrium constant expression. Write the corresponding equation for the dissolution of CaO in an aqueous solution of a strong acid, and relate its equilibrium constant to the previous one.

71. Water that has been saturated with magnesia (MgO) at 25°C has a pH of 10.16. Write a balanced chemical equation for the equilibrium between $MgO(s)$ and the ions it furnishes in aqueous solution, and calculate the equilibrium constant at 25°C. What is the solubility, in moles per liter, of MgO in water?

72. To 1.00 L of a 0.100 M $AgNO_3$ solution is added an excess of sodium chloride. Then 1.00 L of 0.500 M $NH_3(aq)$ is added. Finally, sufficient nitric acid is added until the pH of the resulting solution is 1.0. Write balanced equations for the reactions that take place (if any) at each of three steps in this process.

73. Only about 0.16 mg of $AgBr(s)$ will dissolve in 1.0 L of water (this volume of solid is smaller than the head of a pin). In a solution of ammonia that contains 0.10 mol ammonia per liter of water, there are about 555 water molecules for every molecule of ammonia. However, more than 400 times as much AgBr (68 mg) will dissolve in this solution as in plain water. Explain how such a tiny change in the composition of the solution can have such a large effect on the solubility of AgBr.

* **74.** **(a)** Calculate the solubility of calcium oxalate (CaC_2O_4) in 1.0 M oxalic acid ($H_2C_2O_4$) at 25°C, using the two acid ionization constants for oxalic acid from Table 15.2 and the solubility product $K_{sp} = 2.6 \times 10^{-9}$ for CaC_2O_4.
(b) Calculate the solubility of calcium oxalate in pure water at 25°C.
(c) Account for the difference between the results of (a) and (b).

* **75.** When 6 M HCl is added to solid CdS, some of the solid dissolves to give the complex ion $CdCl_4^{2-}(aq)$.
(a) Write a balanced equation for the reaction that occurs.
(b) Use data from Tables 15.2 and 16.3 and the formation constant of $CdCl_4^{2-}$ ($K_f = 8 \times 10^2$) to calculate the equilibrium constant for the reaction of part (a).
(c) What is the molar solubility of CdS per liter of 6 M HCl?

* **76.** Using data from Table 16.4, calculate the concentrations of $Hg^{2+}(aq)$, $HgCl^+(aq)$, and $HgCl_2(aq)$ that result when 1.00 L of a 0.100 M $Hg(NO_3)_2$ solution is mixed with an equal volume of a 0.100 M $HgCl_2$ solution. (*Hint:* Use the analogy with amphoteric equilibria discussed in Section 10.8.)

* **77.** Calculate the concentration of $Cu^{2+}(aq)$ in a solution that contains 0.020 mol of $CuCl_2$ and 0.100 mol of NaCN in 1.0 L.

$$Cu^{2+}(aq) + 4\,CN^-(aq) \rightleftharpoons Cu(CN)_4^{2-}(aq)$$

$$K = 2.0 \times 10^{30}$$

(*Hint:* Do not overlook the reaction of CN^- with water to give HCN.)

78. An aqueous solution of $K_2[Pt(OH)_6]$ has a pH greater than 7. Explain this fact by writing an equation showing the $Pt(OH)_6^{2-}$ ion acting as a Brønsted–Lowry base and accepting a hydrogen ion from water.

79. In Example 16.10 we included only the first acid dissociation K_{a1} of a 0.100 M aqueous solution of $Fe(H_2O)_6^{3+}$. Subsequent dissociation can also occur, with $K_{a2} = 2.0 \times 10^{-5}$, to give $Fe(H_2O)_4(OH)_2^+$.
(a) Calculate the concentration of $Fe(H_2O)_4(OH)_2^+$ at equilibrium. Does the pH change significantly when this second dissociation is taken into account?
(b) We can describe the same reaction as the dissociation of a complex ion $Fe(OH)_2^+$ to Fe^{3+} and two OH^- ions. Calculate K_f, the formation constant for $Fe(OH)_2^+$.

CUMULATIVE PROBLEMS

80. The volume of a certain saturated solution is greater than the sum of the volumes of the water and salt from which it is made. Predict the effect of increased pressure on the solubility of this salt.

81. Codeine has the molecular formula $C_{18}H_{21}NO_3$. It is soluble in water to the extent of 1.00 g per 120 mL of water at room temperature and 1.00 g per 60 mL of water at 80°C. Compute the molal solubility (in mol kg^{-1}) at both temperatures, taking the density of water to be fixed at 1.00 g cm^{-3}. Is the dissolution of codeine in water endothermic or exothermic?

82. Suppose 1.44 L of a saturated solution of strontium carbonate ($SrCO_3$) in boiling water at 100°C is prepared. The solution is then strongly acidified and shaken to drive off all the gaseous CO_2 that forms. The volume of this gas (at a temperature of 100°C and a partial pressure of 0.972 atm) is measured to be 0.20 L (200 mL).
(a) Calculate the molar solubility of $SrCO_3$ in water at 100°C.
(b) Estimate the solubility product constant K_{sp} of $SrCO_3$ at this temperature.
(c) Explain why the actual K_{sp} at this temperature may be lower than you predicted in part (b).

83. A buffer is prepared by adding 50.0 mL of 0.15 M $HNO_3(aq)$ to 100.0 mL of 0.12 M $NaHCOO(aq)$ (sodium formate). Calculate the solubility of $CaF_2(s)$ in this solution.

CHAPTER 17

Electrochemistry

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Corrosion (rusted iron shown here) has enormous adverse economic consequences. Its prevention requires an understanding of the fundamental underlying chemical processes.

Electrochemistry connects the chemistry of oxidation–reduction reactions to the physics of charge flow. It is the branch of chemistry concerned with the principles and methods for interconverting chemical and electrical energy. Spontaneous chemical reactions can be used as a source of electrical energy; conversely, electrical energy can be used to drive nonspontaneous chemical reactions. The principles of electrochemistry are the foundations for numerous practical applications such as the storage of energy in batteries and the efficient conversion of energy from readily available sources, (e.g., solar or chemical) to other forms useful in technology.

Electrochemistry occurs through redox reactions, and its description requires balanced equations for redox reactions. Both topics are discussed in Section 11.4, which you should review now.

Electrochemical reactions are carried out in devices called **electrochemical cells,** which couple the redox reactions to external electrical circuits. We start our discussion of electrochemistry by using redox reactions in aqueous solution to explain how electrochemical cells operate and relating the current produced in the cell to the stoichiometry of the reaction. Then we apply thermodynamic principles to describe the interconversion of energy in the operation of cells. Because cells operate at constant temperature and pressure, the Gibbs free energy is the most important thermodynamic state function in this description. We relate the change in Gibbs free energy of the redox reaction in the cell to changes in the electrical potential in the external circuit, which in turn measure the capacity of the external circuit to perform electrical work. With this background established, we show how thermodynamics guides the search for new electrochemical technologies. We illustrate practical applications of electrochemical cells in batteries, fuel cells, and the spontaneous corrosion of metals in the environment. We end the chapter by describing practical applications of electrochemical cells in metallurgy and in the electrolysis of water.

17.1 Electrochemical Cells

Electrochemical cells couple oxidation–reduction reactions to external electrical circuits. Electrochemical cells have the fascinating feature that the oxidizing reactant can be physically separate from the reducing reactant as long as they are connected through the external circuit. This is the key feature that allows us to intervene in the conversion between chemical energy and electrical energy. If the reaction is spontaneous, the cell utilizes the Gibbs free energy available from the reaction to convert chemical energy into electrical energy. The electrical energy is provided to the external circuit, where it can perform useful work. This type of cell is called **galvanic. Electrolytic cells** operate in the opposite sense; they take electrical energy from the external circuit and use it to drive reactions that are not spontaneous. In both cases the direction and magnitude of current flow in the external circuit are governed by the Gibbs free energy change of the oxidation–reduction reaction in the cell.

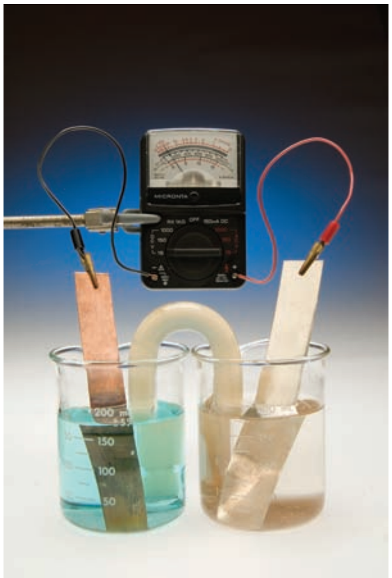

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FIGURE 17.1 A metallic copper anode reacts to give a blue solution containing copper(II) ions as silver ions plate out on a silver cathode in a galvanic cell.

Let's examine a specific case where an electrochemical cell presents an alternative means to carry out a familiar oxidation–reduction reaction. The reaction of copper metal with aqueous silver ions shown in Figure 11.7 is clearly spontaneous. This same reaction can be carried out quite differently without ever bringing the two reactants into *direct* contact with each other if a galvanic cell (a battery) is constructed from them. A copper strip is partially immersed in a solution of $Cu(NO_3)_2$ and a silver strip in a solution of $AgNO_3$, as Figures 17.1 and 17.2 illustrate. The two solutions are connected by a **salt bridge,** which is an inverted U-shaped tube containing a solution of a salt such as $NaNO_3$. The ends of the bridge are stuffed with porous plugs that prevent the two solutions from mixing but allow ions to pass through. The two metal strips are connected to an **ammeter,** an instrument that measures the direction and magnitude of electric current through it.

As copper is oxidized on the left side, Cu^{2+} ions enter the solution. The electrons released in the reaction pass through the external circuit from left to right, as shown by the deflection of the ammeter needle. The electrons enter the silver strip, and at the metal–solution interface, they are picked up by Ag^+ ions, which plate out as atoms on the surface of the silver. This process would lead to an increase of positive charge in the left beaker and a decrease in the right one were it not for the salt bridge; the bridge permits a net flow of positive ions through

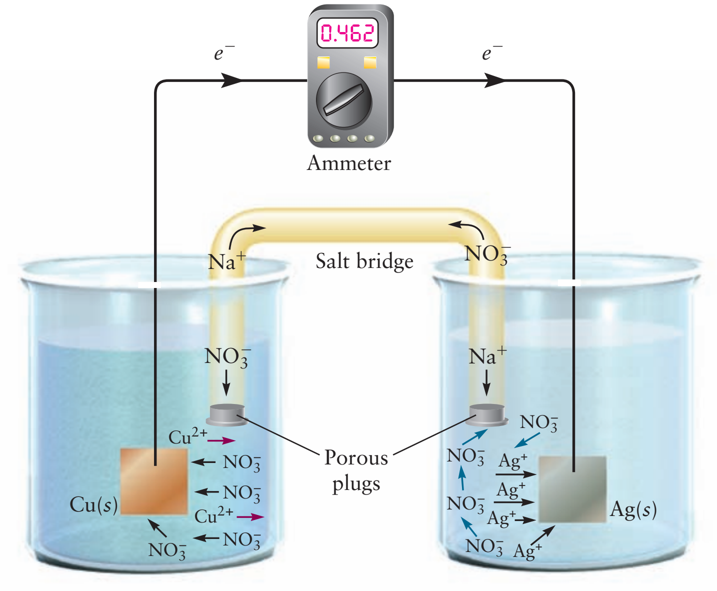


FIGURE 17.2 In the galvanic cell of Figure 17.1, charged particles move when the circuit is completed. Electrons flow from the copper to the silver electrode through the wire. In solution, anions migrate toward the copper electrode and cations move toward the silver electrode. Sodium and nitrate ions migrate through the salt bridge to maintain electrical neutrality.

it into the right beaker and of negative ions into the left beaker, preserving charge neutrality in each.

As discussed in Section 11.4, this oxidation–reduction reaction is composed of two separate half-reactions. The oxidation half-reaction in the left-hand beaker is

$$\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2e^-$$

and the reduction half-reaction in the right beaker is

$$\mathrm{Ag}^+(aq) + e^- \longrightarrow \mathrm{Ag}(s)$$

Following Michael Faraday, chemists call the site at which oxidation occurs in an electrochemical cell the **anode** and the site at which reduction occurs the **cathode.** In the galvanic cell just discussed, copper is the anode (because it is oxidized) and silver is the cathode (because Ag^+ is reduced). Electrons flow in the external circuit from anode to cathode. In solution both positive and negative ions are free to move. In an electrochemical cell, negative ions (anions) move toward the anode and positive ions (cations) move toward the cathode. We will adopt a symbolic representation for galvanic cells in which the anode is shown on the left and the cathode on the right so that electrons flow through the external circuit from left to right. Schematically the copper–silver galvanic cell is represented as

$$\mathrm{Cu}|\mathrm{Cu}^{2+}||\mathrm{Ag}^+|\mathrm{Ag}$$

with the anode on the left and the cathode on the right and with the metal–solution interface represented by | and the salt bridge by ||.

The net chemical reaction in this simple galvanic cell is the same one that takes place when a copper strip is placed in an aqueous solution of silver nitrate (see Fig. 11.7), but there is an essential difference in the process. Because the reaction components are separated into two compartments while electrical continuity is preserved through the external circuit, electrons cannot go directly from copper atoms to silver ions. Electrons are forced to travel through the external circuit (wire) before they ultimately accomplish the same net effect as in Figure 11.7. The current of electrons through the wire can be used for a variety of purposes. A light bulb in the electric circuit would glow from the current passing through it, and the electrochemical cell would have converted chemical energy to electrical energy and ultimately to heat and radiant energy. Or, with a small electric motor in the circuit, the energy change of the chemical reaction can be used to perform mechanical work.

Galvanic and Electrolytic Cells

What causes an electric current to flow in a galvanic cell? There must be an electrical **potential difference,** $\Delta\mathscr{E}$, between two points in the external circuit to cause electrons to flow, just as a difference in gravitational potential between two points on the earth's surface causes water to flow downhill. This electrical potential difference, also called the **cell voltage,** can be measured with an instrument called a **voltmeter;** one lead of the voltmeter is attached to the cathode of the cell and the other lead to the anode. The voltage measured in a galvanic cell depends on the magnitude of the current passing through the cell, and the voltage falls if the current becomes too large. The intrinsic cell voltage (the value at zero current) can be measured by placing a variable voltage source in the external circuit in such a way that its potential difference $\Delta\mathscr{E}_{\text{ext}}$ *opposes* the intrinsic potential difference $\Delta\mathscr{E}$ of the electrochemical cell. The net potential difference is then

$$\Delta\mathscr{E}_{\text{net}} = \Delta\mathscr{E} - \Delta\mathscr{E}_{\text{ext}}$$

$\Delta\mathscr{E}$ can be measured by adjusting $\Delta\mathscr{E}_{\text{ext}}$ until $\Delta\mathscr{E}_{\text{net}}$ becomes 0, at which point the current through the circuit falls to 0 as well. If $\Delta\mathscr{E}_{\text{ext}}$ is held just below $\Delta\mathscr{E}$, the net potential difference becomes small and the cell operation is close to reversible, with only a small current and a slow rate of reaction at the electrodes.

If the opposing external voltage is increased *above* the intrinsic potential difference of the cell, the electrons reverse direction and move toward the copper electrode. Copper ions in solution accept electrons and deposit as copper metal, and silver metal dissolves and furnishes additional Ag^+ ions. The net result is to drive the reverse of the spontaneous reaction, namely,

$$2\ Ag(s) + Cu^{2+}(aq) \longrightarrow 2\ Ag^+ + Cu(s)$$

A galvanic (or voltaic) cell is an electrochemical cell that operates spontaneously. Such a cell converts chemical energy to electrical energy, which can be used to perform work. A cell in which an opposing external potential causes the reaction to occur in the direction opposite the spontaneous direction is called an electrolytic cell; such a cell uses electrical energy provided by the external circuit to carry out chemical reactions that would otherwise not occur. When a galvanic cell is changed into an electrolytic cell by adding an external potential source that reverses the direction of electron flow, the sites of the anode and the cathode are reversed. In the electrolytic cell, oxidation takes place at the silver electrode, which therefore becomes the anode, and the copper electrode becomes the cathode.

EXAMPLE 17.1

The final step in the production of magnesium from seawater is the electrolysis of molten magnesium chloride, in which the overall reaction is

$$Mg^{2+} + 2\ Cl^- \longrightarrow Mg(\ell) + Cl_2(g)$$

Write equations for the half-reactions occurring at the anode and at the cathode, and indicate the direction in which electrons flow through the external circuit.

SOLUTION

The anode is the site at which oxidation takes place, that is, where electrons are given up. The anode half-reaction must be

$$2\ Cl^- \longrightarrow Cl_2(g) + 2\ e^-$$

At the cathode, reduction takes place and the electrons are taken up. The cathode half-reaction is

$$\mathrm{Mg}^{2+} + 2\,e^- \longrightarrow \mathrm{Mg}(\ell)$$

Electrons move from the anode, where chlorine is liberated, through the external circuit to the cathode, where molten magnesium is produced.

Related Problems: 1, 2

Faraday's Laws

The dual aspect of the electrochemical cell—galvanic or electrolytic—was recognized shortly after the cell's discovery in 1800 by Alessandro Volta. Volta constructed a "battery of cells" consisting of a number of plates of silver and zinc that were separated from one another by porous strips of paper saturated with a salt solution. By 1807, Sir Humphry Davy had prepared elemental sodium and potassium by using a battery to electrolyze their respective hydroxides. But, the underlying scientific basis of the electrochemical cell was not understood. Michael Faraday's research showed a direct quantitative relationship between the amounts of substances that react at the cathode and the anode and the total electric charge that passes through the cell. This observation is the substance of **Faraday's laws,** which we state as follows:

1. The mass of a given substance that is produced or consumed at an electrode is proportional to the quantity of electric charge passed through the cell.
2. Equivalent masses[1] of different substances are produced or consumed at an electrode by the passage of a given quantity of electric charge through the cell.

These laws, which summarize the stoichiometry of electrochemical processes, were discovered by Michael Faraday in 1833, more than half a century before the electron was discovered and the atomic basis of electricity was understood.

The charge e on a single electron (expressed in coulombs) has been very accurately determined to be

$$e = 1.60217646 \times 10^{-19}\ \mathrm{C}$$

so the quantity of charge represented by one mole of electrons is

$$\mathscr{Q} = (6.0221420 \times 10^{23}\ \mathrm{mol}^{-1})(1.60217646 \times 10^{-19}\ \mathrm{C}) = 96{,}485.34\ \mathrm{C\ mol}^{-1}$$

This quantity of charge is called the **Faraday constant** (symbol $\mathscr{F}$):

$$\mathscr{F} = 96{,}485.34\ \mathrm{C\ mol}^{-1}$$

Electric current is the amount of charge flowing through a circuit per unit time. If $\mathscr{Q}$ is the magnitude of the charge in coulombs and t is the time in seconds that it takes to pass a point in the circuit, then the current I is

$$I = \frac{\mathscr{Q}}{t} \qquad [17.1]$$

---

[1] The equivalent mass of an element in a redox reaction, or of a compound containing that element, is its molar mass divided by the number of moles of electrons transferred per mole of substance in the corresponding half-reaction.

where the units for I are amperes (A) or coulombs per second. A current of I amperes flowing for t seconds causes It coulombs of charge to pass through the circuit. The number of moles of electrons in that amount of charge is

$$\frac{It}{96{,}485 \text{ C mol}^{-1}} = \text{moles of electrons}$$

From the number of moles of electrons that pass through a circuit, the number of moles (and therefore the number of grams) of substances reacting at the electrodes in the electrochemical cell can be calculated. Suppose a zinc–silver galvanic cell is constructed in which the anode half-reaction is

$$\text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + 2\ e^{-}$$

and the cathode half-reaction is

$$\text{Ag}^{+}(aq) + e^{-} \longrightarrow \text{Ag}(s)$$

Each mole of electrons that passes through the cell arises from the oxidation of $\frac{1}{2}$ mol of Zn(s) (because each Zn atom gives up two electrons) and reduces 1 mol of silver ions. From the molar masses of silver and zinc, we calculate that 65.38/2 = 32.69 g of zinc is dissolved at the anode and 107.87 g of silver is deposited at the cathode. The same relationships hold if the cell is operated as an electrolytic cell, but in that case silver is dissolved and zinc is deposited.

EXAMPLE 17.2

An electrolytic cell is constructed in which the silver ions in silver chloride are reduced to silver at the cathode and copper is oxidized to $\text{Cu}^{2+}(aq)$ at the anode. A current of 0.500 A is passed through the cell for 101 minutes. Calculate the mass of copper metal dissolved and the mass of silver metal deposited.

SOLUTION

$$t = (101 \text{ min})(60 \text{ s min}^{-1}) = 6.06 \times 10^{3} \text{ s}$$

The number of moles of electrons passed through the circuit during this time is

$$\frac{(0.500 \text{ C s}^{-1})(6.06 \times 10^{3} \text{ s})}{96{,}485 \text{ C mol}^{-1}} = 3.14 \times 10^{-2} \text{ mol } e^{-}$$

The half-cell reactions are

$$\text{AgCl}(s) + e^{-} \longrightarrow \text{Ag}(s) + \text{Cl}^{-}(aq) \qquad \text{(cathode)}$$

$$\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + 2\ e^{-} \qquad \text{(anode)}$$

so the masses of silver deposited and copper dissolved are

$$(3.14 \times 10^{-2} \text{ mol } e^{-}) \times \left(\frac{1 \text{ mol Ag}}{1 \text{ mol } e^{-}}\right) \times (107.78 \text{ g mol}^{-1}) = 3.39 \text{ g Ag deposited}$$

$$(3.14 \times 10^{-2} \text{ mol } e^{-}) \times \left(\frac{1 \text{ mol Cu}}{2 \text{ mol } e^{-}}\right) \times (63.55 \text{ g mol}^{-1}) = 0.998 \text{ g Cu dissolved}$$

Related Problems: 3, 4, 5, 6

17.2 The Gibbs Free Energy and Cell Voltage

Chapters 12 and 13 discussed the pressure–volume work associated with expanding and compressing gases. In electrochemistry a different kind of work, **electrical work,** is fundamental. If an amount of charge, Q, moves through a potential difference $\Delta\mathscr{E}$, the electrical work is

$$w_{\text{elec}} = -Q\,\Delta\mathscr{E} \qquad [17.2]$$

The minus sign appears in this equation because the same thermodynamic convention is followed as in Chapters 12 and 13—that work done by the system (here, an electrochemical cell) has a negative sign. Because work is measured in joules and charge in coulombs, $\Delta\mathcal{E}$ has units of joules per coulomb. One volt (abbreviated V) is 1 joule per coulomb. Because the total charge Q is the current I multiplied by the time t in seconds during which the current is flowing, this equation for the electrical work can also be written

$$w_{\text{elec}} = -It\,\Delta\mathcal{E}$$

The potential difference $\Delta\mathcal{E}$ is positive for a galvanic cell, so w_{elec} is negative in this case and net electrical work is performed by the galvanic cell. In an electrolytic cell, in contrast, $\Delta\mathcal{E}$ is negative and w_{elec} is positive, corresponding to net electrical work done on the system by an external source such as an electric generator.

EXAMPLE 17.3

A 6.00-V battery delivers a steady current of 1.25 A for a period of 1.50 hours. Calculate the total charge Q, in coulombs, that passes through the circuit and the electrical work done *by* the battery.

SOLUTION

The total charge is

$$Q = It = (1.25\text{ C s}^{-1})(1.50\text{ hr})(3600\text{ s hr}^{-1}) = 6750\text{ C}$$

The electrical work is

$$w_{\text{elec}} = -Q\,\Delta\mathcal{E} = -(6750\text{ C})(6.00\text{ J C}^{-1}) = -4.05 \times 10^4\text{ J}$$

This is the work done *on* the battery, so the work done *by* the battery is the negative of this, or +40.5 kJ.

Thermodynamics demonstrates a fundamental relationship between the change in free energy, ΔG, of a spontaneous chemical reaction at constant temperature and pressure, and the maximum electrical work that such a reaction is capable of producing:

$$-w_{\text{elec,max}} = |\Delta G| \qquad \text{(at constant } T \text{ and } P) \tag{17.3}$$

To show this, recall the definition of the Gibbs free energy function G:

$$G = H - TS = U + PV - TS$$

For processes at constant pressure P and constant temperature T (the usual case in electrochemical cells),

$$\Delta G = \Delta U + P\,\Delta V - T\,\Delta S$$

From the first law of thermodynamics,

$$\Delta U = q + w$$

or

$$\Delta U = q + w_{\text{elec}} - P\,\Delta V$$

because there are now two kinds of work, electrical work w_{elec} and pressure–volume work $-P_{\text{ext}}\,\Delta V = -P\,\Delta V$. Combining this with the equation for the change in free energy gives

$$\Delta G = q + w_{\text{elec}} - P\,\Delta V + P\,\Delta V - T\,\Delta S = q + w_{\text{elec}} - T\,\Delta S$$

If the condition of reversibility is imposed upon the galvanic cell, then

$$q = q_{\text{rev}} = T\,\Delta S$$

and the free energy change is

$$\Delta G = w_{\text{elec,rev}}$$

In the same cell operated irreversibly (i.e., with a large current permitted to flow), less electrical work is accomplished. The maximum electrical work is done by the galvanic cell when it is operated reversibly.

If n mol of electrons (or $n\mathcal{F}$ coulombs of charge) passes through the external circuit of the galvanic cell when it is operated reversibly, and if $\Delta\mathcal{E}$ is the reversible cell voltage, then

$$\Delta G = w_{\text{elec}} = -Q\,\Delta\mathcal{E} = -n\mathcal{F}\,\Delta\mathcal{E} \qquad \text{(reversible)}$$

Electrical work is produced by an electrochemical cell only if $\Delta G < 0$, or when $\Delta\mathcal{E} > 0$, which amounts to the same thing. This relationship provides a direct way to determine free energy changes for chemical reactions from measurements of cell voltage.

Standard States and Cell Voltages

Recall from Chapters 12 and 13 that the *standard state* of a substance means a pressure of 1 atm and a specified temperature. In addition, the standard state of a solute is that for which its concentration in ideal solution is 1 M.[2] The standard free energy change $\Delta G°$ for a reaction in which all reactants and products are in their standard states can be calculated from a table of standard free energies of formation $\Delta G_f°$ of the substances taking part in the reaction (see Appendix D). For reactions that can be carried out in electrochemical cells, the standard free energy change $\Delta G°$ is related to a **standard cell voltage** $\Delta\mathcal{E}°$ by

$$\Delta G° = -n\mathcal{F}\,\Delta\mathcal{E}° \qquad [17.4]$$

Here $\Delta\mathcal{E}°$ is the cell voltage (potential difference) of a galvanic cell in which reactants and products are in their standard states (gases at 1 atm pressure, solutes at 1 M concentration, metals in their pure stable states, and a specified temperature). This standard cell voltage is an intrinsic electrical property of the cell, which can be calculated from the standard free energy change $\Delta G°$ by means of Equation 17.4. Conversely, $\Delta G°$ (and hence equilibrium constants for cell reactions) can be determined by measuring the standard cell voltage $\Delta\mathcal{E}°$ of a reaction in which n mol of electrons passes through the external circuit.

EXAMPLE 17.4

A $Zn^{2+}|Zn$ half-cell is connected to a $Cu^{2+}|Cu$ half-cell to make a galvanic cell, in which $[Zn^{2+}] = [Cu^{2+}] = 1.00$ M. The cell voltage at 25°C is measured to be $\Delta\mathcal{E}° = 1.10$ V, and Cu is observed to plate out as the reaction proceeds. Calculate $\Delta G°$ for the chemical reaction that takes place in the cell, for 1.00 mol of zinc dissolved.

SOLUTION

The reaction is

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

---

[2] Recall that the standard state of a solute has unit activity, which can differ significantly from 1 M concentration for a real electrolyte solution. In what follows, we will nevertheless refer to 1 M concentration as the standard state.

because Cu is a product. For the reaction as written, in which 1 mol of Zn(*s*) and 1 mol of $Cu^{2+}(aq)$ react, 2 mol of electrons passes through the external circuit, so $n = 2$. Therefore,

$$\Delta G° = -n\mathscr{F}\,\Delta\mathscr{E}° = -(2.00 \text{ mol})(96{,}485 \text{ C mol}^{-1})(1.10 \text{ V})$$
$$= -2.12 \times 10^5 \text{ J} = -212 \text{ kJ}$$

Related Problems: 11, 12

Half-Cell Voltages

We could tabulate all the conceivable galvanic cells and their standard voltages, but the list would be very long. To avoid this, the half-cell reduction potentials $\mathscr{E}°$ are tabulated; they can be combined to obtain the standard cell voltage $\Delta\mathscr{E}°$ for any complete cell.

To see this, return to the standard cell just considered, made up of $Zn^{2+}|Zn$ and $Cu^{2+}|Cu$ half-cells. Each half-cell reaction is written as a reduction:

$$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$$
$$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$$

Each half-reaction has a certain tendency to occur. If **reduction potentials** $\mathscr{E}°(Zn^{2+}|Zn)$ and $\mathscr{E}°(Cu^{2+}|Cu)$ are associated with the two half-cells, the magnitude and sign of each of these potentials are related to the tendency of the reaction to occur as written. The more positive the half-cell reaction's potential, the greater its tendency to take place as a reduction. Of course, a single half-cell reduction reaction cannot take place in isolation because a source of electrons is required. This can be achieved only by combining two half-cells. When two half-cells are combined, the reaction that has the more positive (or algebraically greater) reduction potential occurs as a reduction, and the one with the less positive potential is forced to run in reverse (as an oxidation) to supply electrons. The net cell potential (voltage) is then the *difference* between the individual half-cell reduction potentials. In the preceding example, copper is observed to plate out on the cathode, so its potential must be more positive than that of zinc:

$$\Delta\mathscr{E}° = \mathscr{E}°(Cu^{2+}|Cu) - \mathscr{E}°(Zn^{2+}|Zn) = 1.10 \text{ V}$$

When two half-cells are combined to make a galvanic cell, reduction occurs in the half-cell with the algebraically greater potential (making it the cathode) and oxidation occurs in the other half-cell (making it the anode). We therefore write

$$\boxed{\Delta\mathscr{E}° = \mathscr{E}°(\text{cathode}) - \mathscr{E}°(\text{anode})} \qquad [17.5]$$

for a galvanic cell. Cell voltages and half-cell reduction potentials are *intensive* quantities, independent of the amount of matter in a cell or the amount reacting. Half-cell reduction potentials are therefore *not* multiplied by numbers of moles reacting (as Gibbs free energies would be) to obtain the overall cell potential.

In thermodynamics, only energy differences are measurable; absolute energies are not. Therefore, energies (or enthalpies or free energies) are defined relative to a reference state for which these quantities are arbitrarily set at 0 by international agreement. The same reasoning applies to half-cells: Because only differences are measured, we are free to define a reference reduction potential for a particular half-cell and measure other half-cell reduction potentials relative to it. The convention used is to define $\mathscr{E}°$ for the half-cell reduction of $H_2(g)$ to $H_3O^+(aq)$ to be 0 at all temperatures, when the gas pressure at the electrode is 1 atm and the $H_3O^+(aq)$ concentration in solution is 1 M (Fig. 17.3).

$$2\,H_3O^+(aq) + 2\,e^- \longrightarrow H_2(g) + 2\,H_2O(\ell) \qquad \mathscr{E}° = 0 \text{ V (by definition)}$$

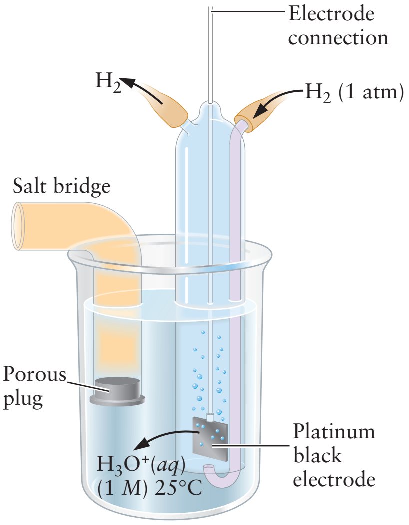


FIGURE 17.3 Hydrogen is a gas at room conditions, and electrodes cannot be constructed from it directly. In the hydrogen half-cell shown here, a piece of platinum covered with a fine coating of platinum black is dipped into the solution, and a stream of hydrogen is passed over the surface. The platinum itself does not react but provides a support surface for the reaction of the H_2 and water to give H_3O^+, or the reverse. It also provides the necessary electrical connection to carry away or supply electrons.

All other half-cell potentials are then determined from this reference potential by combining their standard half-cells with the standard $H_3O^+|H_2$ half-cell in a galvanic cell and measuring the cell voltage. The magnitude and sign of that cell voltage give the standard potential of the half-cell in question, its reaction being written as an oxidation or a reduction according to whether the electrode behaves as the anode or the cathode of the galvanic cell.

For example, if a $Cu^{2+}(1\ \text{M})|Cu$ half-cell is connected to the standard $H_3O^+(1\ \text{M})|H_2$ half-cell, copper is observed to plate out; therefore the copper half-cell is the cathode and the hydrogen half-cell is the anode. The observed cell voltage is 0.34 V; thus,

$$\begin{aligned}\Delta\mathcal{E}^\circ &= \mathcal{E}^\circ(\text{cathode}) - \mathcal{E}^\circ(\text{anode})\\ &= \mathcal{E}^\circ(Cu^{2+}|Cu) - \mathcal{E}^\circ(H_3O^+|H_2) = \mathcal{E}^\circ(Cu^{2+}|Cu) - 0\\ &= 0.34\text{ V}\end{aligned}$$

Therefore, the standard $Cu^{2+}|Cu$ half-cell potential is 0.34 V on a scale in which the standard $H_3O^+|H_2$ half-cell potential is 0:

$$Cu^{2+}(1\ \text{M}) + 2\,e^- \longrightarrow Cu(s) \qquad \mathcal{E}^\circ = 0.34\text{ V}$$

When a $Zn^{2+}(1\ \text{M})|Zn$ half-cell is connected to the standard hydrogen half-cell, zinc dissolves; its half-cell is the anode because oxidation occurs in it. The measured cell voltage is 0.76 V, so

$$\Delta\mathcal{E}^\circ = 0.76\text{ V} = \mathcal{E}^\circ(\text{cathode}) - \mathcal{E}^\circ(\text{anode}) = 0 - \mathcal{E}^\circ(Zn^{2+}|Zn)$$

The $Zn^{2+}(1\ \text{M})|Zn$ half-cell reduction potential is therefore −0.76 V:

$$Zn^{2+}(1\ \text{M}) + 2\,e^- \longrightarrow Zn(s) \qquad \mathcal{E}^\circ = -0.76\text{ V}$$

If the zinc and copper half-cells are combined, the copper half-cell will be the cathode because it has the more positive half-cell reduction potential. The galvanic cell voltage under standard-state conditions (Fig. 17.4) will be

$$\Delta\mathcal{E}^\circ = \mathcal{E}^\circ(\text{cathode}) - \mathcal{E}^\circ(\text{anode}) = 0.34\text{ V} - (-0.76\text{ V}) = 1.10\text{ V}$$

in agreement with the measured value.

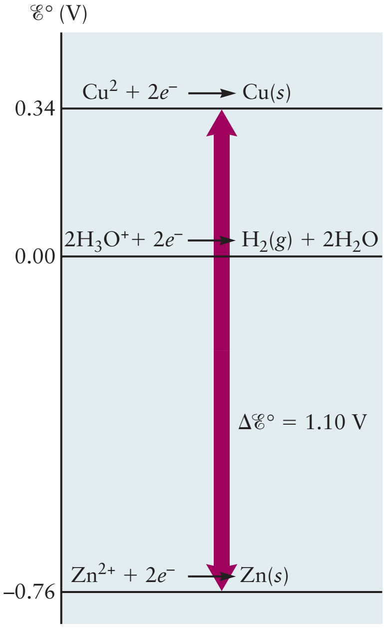


FIGURE 17.4 Sometimes standard reduction potentials are represented to scale. In this diagram the distance between a pair of standard half-cell potentials is proportional to the $\Delta\mathcal{E}^\circ$ generated by the electrochemical cell that combines the two. The half-reaction with the higher reduction potential forces the other half-reaction to occur in the reverse direction.

EXAMPLE 17.5

An aqueous solution of potassium permanganate ($KMnO_4$) appears deep purple. In aqueous acidic solution, the permanganate ion can be reduced to the pale-pink manganese(II) ion (Mn^{2+}). Under standard conditions, the reduction potential of an $MnO_4^-|Mn^{2+}$ half-cell is $\mathcal{E}^\circ = 1.49$ V. Suppose this half-cell is combined with a $Zn^{2+}|Zn$ half-cell in a galvanic cell, with $[Zn^{2+}] = [MnO_4^-] = [Mn^{2+}] = [H_3O^+] = 1\ \text{M}$. **(a)** Write equations for the reactions at the anode and the cathode. **(b)** Write a balanced equation for the overall cell reaction. **(c)** Calculate the standard cell potential difference, $\Delta\mathcal{E}^\circ$.

SOLUTION

(a) Because $\mathcal{E}^\circ(MnO_4^-|Mn^{2+}) = 1.49$ V is more positive than $\mathcal{E}^\circ(Zn^{2+}|Zn) = -0.76$ V, permanganate ions will be reduced at the cathode. The balanced half-cell reaction requires the presence of H_3O^+ ions and water, giving

$$MnO_4^-(aq) + 8\,H_3O^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 12\,H_2O(\ell)$$

The half-equation for the oxidation of Zn at the anode is

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$$

(b) In the overall reaction, the number of electrons taken up at the cathode must equal the number released at the anode, so the first equation must be multiplied by 2 and the second by 5. Adding the two gives the overall reaction:

$$2\,MnO_4^-(aq) + 16\,H_3O^+(aq) + 5\,Zn(s) \longrightarrow 2\,Mn^{2+}(aq) + 24\,H_2O(\ell) + 5\,Zn^{2+}(aq)$$

(c) The galvanic cell potential is the difference between the standard reduction potential for permanganate (at the cathode) and that for zinc (at the anode):

$$\Delta\mathscr{E}° = \mathscr{E}°(MnO_4^-|Mn^{2+}) - \mathscr{E}°(Zn^{2+}|Zn) = 1.49 - (-0.76) = 2.25\ V$$

Note that the half-cell potentials are not multiplied by their coefficients (2 and 5) before subtraction. Half-cell potentials are *intensive* properties of a galvanic cell and are therefore independent of the amount of the reacting species.

Related Problems: 13, 14

Appendix E summarizes the standard reduction potentials for a large number of half-reactions. The table lists the reactions in order of decreasing reduction potentials—that is, with the most positive at the top and the most negative at the bottom. In any galvanic cell, the half-cell that is listed higher in the table will act as the cathode (if both half-cells are in the standard state).

A strong **oxidizing agent** is a chemical species that is itself easily reduced. Such species are marked by large positive reduction potentials and appear at the top left in Appendix E. Fluorine has the largest reduction potential listed, and fluorine molecules are extremely eager to accept electrons to become fluoride ions. Other strong oxidizing agents include hydrogen peroxide (H_2O_2) and solutions of permanganate ion (MnO_4^-). A strong **reducing agent,** on the other hand, is easily oxidized, so its corresponding reduction potential is large and negative. Such reducing agents appear at the lower right in Appendix E. The alkali and alkaline earth metals are especially good reducing agents.

Oxygen itself is a good oxidizing agent in acidic solution at pH 0 because it has a fairly high reduction potential:

$$O_2(g) + 4\ H_3O^+(aq) + 4\ e^- \longrightarrow 6\ H_2O(\ell) \qquad \mathscr{E}° = 1.229\ V$$

Ozone (O_3) is still stronger because its high free energy relative to oxygen provides an additional driving force for oxidation reactions, as shown by its high half-cell reduction potential in acidic aqueous solution:

$$O_3(g) + 2\ H_3O^+(aq) + 2\ e^- \longrightarrow O_2 + 3\ H_2O(\ell) \qquad \mathscr{E}° = 2.07\ V$$

Because of its great oxidizing power, ozone is used commercially as a bleach for wood pulp and as a disinfectant and sterilizing agent for water, where it oxidizes algae and organic impurities but leaves no undesirable residue. In basic aqueous solution, the half-reactions of oxygen-containing species involve hydroxide ions instead of hydronium ions, and the reduction potentials are correspondingly changed. At pH 14 (standard basic conditions),

$$O_2(g) + 2\ H_2O(\ell) + 4\ e^- \longrightarrow 4\ OH^-(aq) \qquad \mathscr{E}° = 0.401\ V$$

$$O_3(g) + H_2O(\ell) + 2\ e^- \longrightarrow O_2 + 2\ OH^-(aq) \qquad \mathscr{E}° = 1.24\ V$$

Both oxygen and ozone are less effective oxidizing agents in basic solutions than in acidic solutions.

Adding and Subtracting Half-Cell Reactions

When two half-cells are combined to form a galvanic cell, their half-cell potentials are *not* multiplied by the coefficients that appear in the overall balanced chemical equation. This shows that potentials cannot be combined as thermodynamic state functions are, because potentials are intensive rather than extensive properties. The same observation applies when two half-cells are combined to obtain *another half-cell*. For example, suppose we wish to know the standard half-cell potential corresponding to the reaction

$$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$$

when the standard half-cell potentials are known for the reactions

$$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s) \qquad \mathcal{E}_1^\circ = \mathcal{E}^\circ(Cu^{2+}|Cu) = 0.340 \text{ V}$$

$$Cu^{+}(aq) + e^- \longrightarrow Cu(s) \qquad \mathcal{E}_2^\circ = \mathcal{E}^\circ(Cu^{+}|Cu) = 0.522 \text{ V}$$

Could we not simply subtract the second half-reaction from the first and, correspondingly, the second half-cell potential from the first half-cell potential, to obtain

$$Cu^{2+}(aq) + e^- \longrightarrow Cu^{+}(aq) \qquad \mathcal{E}_3^\circ = \mathcal{E}^\circ(Cu^{2+}|Cu^{+}) = -0.182 \text{ V?}$$

The answer is "No." Instead, the *free energy change* for each half-reaction must be calculated from

$$\Delta G_{\text{hc}}^\circ = -n_{\text{hc}}\mathcal{F}\mathcal{E}^\circ$$

and combined before calculating $\mathcal{E}^\circ$ for their resultant. Thus, for the free energy change for the difference of the two half-reactions,

$$\Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ = -n_1\mathcal{F}\mathcal{E}_1^\circ + n_2\mathcal{F}\mathcal{E}_2^\circ$$

Setting this equation equal to $-n_3\mathcal{F}\mathcal{E}_3^\circ$ gives

$$-n_3\mathcal{F}\mathcal{E}_3^\circ = -n_1\mathcal{F}\mathcal{E}_1^\circ + n_2\mathcal{F}\mathcal{E}_2^\circ$$

$$\mathcal{E}_3^\circ = \frac{n_1\mathcal{E}_1^\circ - n_2\mathcal{E}_2^\circ}{n_3}$$

The correct standard half-cell potential for the half-cell reaction

$$Cu^{2+}(aq) + e^- \longrightarrow Cu^{+}(aq)$$

is

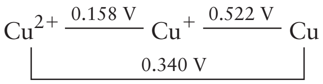
$$\mathcal{E}^\circ(Cu^{2+}|Cu^{+}) = \frac{(2 \text{ mol})(0.340 \text{ V}) - (1 \text{ mol})(0.522 \text{ V})}{1 \text{ mol}} = 0.158 \text{ V}$$

This same procedure using free energies can be used to calculate overall cell voltages from half-cell potentials. Here, the number of moles of electrons n_1 released at the anode is equal to the number n_2 taken up at the cathode and is the number n_3 implied by the overall chemical equation. The electrons then cancel out, and the result reduces to the simple form found before:

$$\Delta\mathcal{E}^\circ = \mathcal{E}^\circ(\text{cathode}) - \mathcal{E}^\circ(\text{anode})$$

Reduction Potential Diagrams and Disproportionation

We can summarize the half-reactions of copper in a **reduction potential diagram** of the form



The line connecting each pair of species stands for the entire half-reaction, written as a reduction and balanced by the addition of electrons (and, where necessary, water and H_3O^+ or OH^-). The number over each line is the corresponding reduction potential in volts.

Recall from Example 11.10 that *disproportionation* is the process in which a single substance is both oxidized and reduced. Reduction potential diagrams enable us to determine which species are stable with respect to disproportionation.

A species can disproportionate if and only if a reduction potential that lies immediately to its right is larger than one that appears immediately to its left. To demonstrate this, note that a disproportionation reaction is the sum of a reduction half-reaction and an oxidation half-reaction. The driving force is the *difference* between the two reduction potentials, and if this difference is positive the disproportionation occurs spontaneously. In the case of Cu^+, the disproportionation reaction is

$$2\ Cu^+ \longrightarrow Cu^{2+} + Cu(s) \qquad \Delta\mathscr{E}° = 0.522 - 0.158 = 0.364\text{ V}$$

Because $\Delta\mathscr{E}° > 0$, $\Delta G° < 0$ and the reaction occurs spontaneously, although the rate may be slow.

EXAMPLE 17.6

Hydrogen peroxide, H_2O_2, is a possible product of the reduction of oxygen in acidic solution:

$$O_2 + 2\ H_3O^+ + 2\ e^- \longrightarrow H_2O_2 + 2\ H_2O \qquad \mathscr{E}_3° = ?$$

It can then be further reduced to water:

$$H_2O_2 + 2\ H_3O^+ + 2\ e^- \longrightarrow 4\ H_2O \qquad \mathscr{E}_3° = 1.77\text{ V}$$

(a) Use the half-cell potential just given for the reduction of H_2O_2, together with that given earlier,

$$O_2 + 4\ H_3O^+ + 4\ e^- \longrightarrow 6\ H_2O \qquad \mathscr{E}_1° = 1.229\text{ V}$$

to calculate the standard half-cell potential for the reduction of O_2 to H_2O_2 in acidic solution.

(b) Write a reduction potential diagram for O_2, H_2O_2, and H_2O.

(c) Is H_2O_2 stable with respect to disproportionation in acidic solution?

SOLUTION

(a) The desired half-cell reaction is obtained by *subtracting* the reaction with potential $\mathscr{E}_2°$ from that with potential $\mathscr{E}_1°$. The half-cell reduction potentials are not subtracted, however, but rather combined as described earlier in this section. Taking $n_1 = 4$, $n_2 = 2$, and $n_3 = 2$ gives

$$\mathscr{E}_3° = \frac{n_1\mathscr{E}_1° - n_2\mathscr{E}_2°}{n_3}$$

$$= \frac{(4\text{ mol})(1.229\text{ V}) - (2\text{ mol})(1.77\text{ V})}{2\text{ mol}} = 0.69\text{ V}$$

(b) The reduction potential diagram is obtained by omitting the electrons, water, and H_3O^+ from the corresponding half-equations:

$$\begin{tikzcd} O_2 \arrow[r, dash, "0.69\text{ V}"] \arrow[rr, dash, bend right, "1.229\text{ V}"'] & H_2O_2 \arrow[r, dash, "1.77\text{ V}"] & H_2O \end{tikzcd}$$

(c) H_2O_2 is thermodynamically unstable to disproportionation in acidic solution because the half-cell potential to its right (1.77 V) is higher than that to its left (0.69 V). The disproportionation of H_2O_2 is also spontaneous in neutral solution, but it is slow enough that aqueous solutions of hydrogen peroxide can be stored for a long time without deteriorating, as long as they are kept out of the light.

Related Problems: 23, 24, 25, 26

17.3 Concentration Effects and the Nernst Equation

In real-world applications, concentrations and pressures are rarely conveniently fixed at their standard state values. It is thus necessary to understand how concentration and pressure affect the cell voltage by applying the thermodynamic principles of Chapter 14 to electrochemical cells. In Chapter 14, we showed that the free energy change is related to the reaction quotient Q through

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Combining this equation with

$$\Delta G = -n\mathcal{F}\,\Delta\mathcal{E}$$

and

$$\Delta G^\circ = -n\mathcal{F}\,\Delta\mathcal{E}^\circ$$

gives

$$-n\mathcal{F}\,\Delta\mathcal{E} = -n\mathcal{F}\,\Delta\mathcal{E}^\circ + RT \ln Q$$

and

$$\boxed{\Delta\mathcal{E} = \Delta\mathcal{E}^\circ - \frac{RT}{n\mathcal{F}} \ln Q} \qquad [17.6]$$

which is known as the **Nernst equation.**

The Nernst equation can be rewritten in terms of common (base-10) logarithms by using the fact that

$$\ln Q \approx 2.303 \log_{10} Q$$

At 25°C (298.15 K), the combination of constants $2.303\, RT/\mathcal{F}$ becomes

$$2.3\,\frac{RT}{\mathcal{F}} = (2.3)\left[\frac{(8.315 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{96{,}485 \text{ C mol}^{-1}}\right]$$

$$= 0.0592 \text{ J C}^{-1} = 0.0592 \text{ V}$$

because 1 joule per coulomb is 1 volt. The Nernst equation then becomes

$$\boxed{\Delta\mathcal{E} = \Delta\mathcal{E}^\circ - \frac{0.0592 \text{ V}}{n} \log_{10} Q \quad (\text{at } 25^\circ\text{C})} \qquad [17.7]$$

which is its most familiar form. Here n is the number of moles of electrons transferred in the overall chemical reaction as written, and V signifies the units of the constant 0.0592. In a galvanic cell made from zinc, aluminum, and their ions,

$$\begin{array}{r}
3\,\text{Zn}^{2+}(aq) + 6\,e^- \longrightarrow 3\,\text{Zn}(s) \\
2\,\text{Al}(s) \longrightarrow 2\,\text{Al}^{3+}(aq) + 6\,e^- \\
\hline
3\,\text{Zn}^{2+}(aq) + 2\,\text{Al}(s) \longrightarrow 2\,\text{Al}^{3+}(aq) + 3\,\text{Zn}(s)
\end{array}$$

there is a net transfer of $n = 6$ mol of electrons through the external circuit for the equation as written.

The Nernst equation applies to half-cells in exactly the same way as it does to complete electrochemical cells. For any half-cell potential at 25°C,

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0592 \text{ V}}{n_{\text{hc}}} \log_{10} Q_{\text{hc}}$$

where n_{hc} is the number of electrons appearing in the half-reaction and Q_{hc} is the reaction quotient for the half-cell reaction written as a reduction. The electrons themselves do not appear in Q_{hc}. In the $Zn^{2+}|Zn$ case, the half-reaction written as a reduction is

$$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$$

so $n_{hc} = 2$ and $Q_{hc} = 1/[Zn^{2+}]$. If two half-cells in which reactants and products are not in their standard states are combined in a galvanic cell, the one with the more positive value of $\mathcal{E}$ will be the cathode, where reduction takes place, and the cell voltage will be

$$\Delta\mathcal{E} = \mathcal{E}(\text{cathode}) - \mathcal{E}(\text{anode})$$

EXAMPLE 17.7

Suppose the $Zn|Zn^{2+}||MnO_4^-|Mn^{2+}$ cell from Example 17.5 is operated at pH 2.00 with $[MnO_4^-] = 0.12$ M, $[Mn^{2+}] = 0.0010$ M, and $[Zn^{2+}] = 0.015$ M. Calculate the cell voltage $\Delta\mathcal{E}$ at 25°C.

SOLUTION

Recall that the overall equation for this cell is

$$2\,MnO_4^-(aq) + 5\,Zn(s) + 16\,H_3O^+(aq) \longrightarrow 2\,Mn^{2+}(aq) + 5\,Zn^{2+}(aq) + 24\,H_2O(\ell)$$

From Example 17.5, for every 5 mol of Zn oxidized (or 2 mol of MnO_4^- reduced), 10 mol of electrons passes through the external circuit, so $n = 10$. A pH of 2.00 corresponds to a hydronium ion concentration of 0.010 M. Putting this and the other concentrations into the expression for the reaction quotient and substituting both Q and the value of $\Delta\mathcal{E}°$ (from Example 17.5) into the Nernst equation give

$$\begin{aligned}\Delta\mathcal{E} &= 2.25\text{ V} - \frac{0.0592\text{ V}}{10}\log_{10}\frac{[Mn^{2+}]^2[Zn^{2+}]^5}{[MnO_4^-]^2[H_3O^+]^{16}} \\ &= 2.25\text{ V} - \frac{0.0592\text{ V}}{10}\log_{10}\frac{(0.0010)^2(0.015)^5}{(0.12)^2(0.010)^{16}} \\ &= 2.25\text{ V} - \frac{0.0592\text{ V}}{10}\log_{10}(5.3\times10^{18}) = 2.14\text{ V}\end{aligned}$$

Related Problems: 27, 28

Measuring Equilibrium Constants

Electrochemistry provides a convenient and accurate way to measure equilibrium constants for many solution-phase reactions. For an overall cell reaction,

$$\Delta G° = -n\mathcal{F}\,\Delta\mathcal{E}°$$

In addition, $\Delta G°$ is related to the equilibrium constant K through

$$\Delta G° = -RT\ln K$$

so

$$RT\ln K = n\mathcal{F}\,\Delta\mathcal{E}°$$

$$\ln K = \frac{n\mathcal{F}}{RT}\Delta\mathcal{E}°$$

$$\log_{10}K = \frac{n}{0.0592\text{ V}}\Delta\mathcal{E}° \qquad \text{(at 25°C)} \qquad [17.8]$$

The same result can be obtained in a slightly different way. Return to the Nernst equation, which reads (at 25°C)

$$\Delta\mathscr{E} = \Delta\mathscr{E}° - \frac{0.0592\ \text{V}}{n}\log_{10} Q$$

Suppose all species are present under standard-state conditions; then $Q = 1$ initially and the cell voltage $\Delta\mathscr{E}$ is the standard cell voltage $\Delta\mathscr{E}°$. As the reaction takes place, Q increases and $\Delta\mathscr{E}$ decreases. As reactants are used up and products are formed, the cell voltage approaches 0. Eventually, equilibrium is reached and $\Delta\mathscr{E}$ becomes 0. At that point,

$$\Delta\mathscr{E}° = \frac{0.0592\ \text{V}}{n}\log_{10} K$$

which is the same as the relationship just obtained. This relation lets us calculate equilibrium constants from standard cell voltages, as the following example illustrates.

EXAMPLE 17.8

Calculate the equilibrium constant for the redox reaction

$$2\ \text{MnO}_4^-(aq) + 5\ \text{Zn}(s) + 16\ \text{H}_3\text{O}^+(aq) \longrightarrow 2\ \text{Mn}^{2+}(aq) + 5\ \text{Zn}^{2+}(aq) + 24\ \text{H}_2\text{O}(\ell)$$

at 25°C using the cell voltage calculated in Example 17.5.

SOLUTION

From Example 17.5, $\Delta\mathscr{E}° = 2.25$ V, and from the analysis there and in Example 17.7, $n = 10$ for the preceding reaction. Therefore,

$$\log_{10} K = \frac{n}{0.0592\ \text{V}}\Delta\mathscr{E}° = \frac{10}{0.0592\ \text{V}}(2.25\ \text{V}) = 380$$

$$K = 10^{380}$$

This overwhelmingly large equilibrium constant reflects the strength of permanganate ion as an oxidizing agent and of zinc as a reducing agent. It means that for all practical purposes no MnO_4^- ions are present at equilibrium.

Related Problems: 35, 36

The foregoing example illustrates how equilibrium constants for overall cell reactions can be determined electrochemically. Although the example dealt with redox equilibrium, related procedures can be used to measure the solubility product constants of sparingly soluble ionic compounds or the ionization constants of weak acids and bases. Suppose that the solubility product constant of AgCl is to be determined by means of an electrochemical cell. One half-cell contains solid AgCl and Ag metal in equilibrium with a known concentration of $\text{Cl}^-(aq)$ (established with 0.00100 M NaCl, for example) so that an unknown but definite concentration of $\text{Ag}^+(aq)$ is present. A silver electrode is used so that the half-cell reaction involved is either the reduction of $\text{Ag}^+(aq)$ or the oxidation of Ag. This is, in effect, an $\text{Ag}^+|\text{Ag}$ half-cell whose potential is to be determined. The second half-cell can be any whose potential is accurately known, and its choice is a matter of convenience. In the following example, the second half-cell is a standard $\text{H}_3\text{O}^+|\text{H}_2$ half-cell.

EXAMPLE 17.9

A galvanic cell is constructed using a standard hydrogen half-cell (with platinum electrode) and a half-cell containing silver and silver chloride:

$$\mathrm{Pt}|\mathrm{H_2}(1\ \mathrm{atm})|\mathrm{H_3O^+}(1\ \mathrm{M})||\mathrm{Cl^-}(1.00 \times 10^{-3}\ \mathrm{M}) + \mathrm{Ag^+}(?\ \mathrm{M})|\mathrm{AgCl}|\mathrm{Ag}$$

The $H_2|H_3O^+$ half-cell is observed to be the anode, and the measured cell voltage is $\Delta\mathscr{E} = 0.397$ V. Calculate the silver ion concentration in the cell and the K_{sp} of AgCl at 25°C.

SOLUTION

The half-cell reactions are

$$\mathrm{H_2}(g) + 2\ \mathrm{H_2O}(\ell) \longrightarrow 2\ \mathrm{H_3O^+}(aq) + 2\ e^- \qquad \text{(anode)}$$

$$2\ \mathrm{Ag^+}(aq) + 2\ e^- \longrightarrow 2\ \mathrm{Ag}(s) \qquad \text{(cathode)}$$

$$\Delta\mathscr{E}° = \mathscr{E}°(\text{cathode}) - \mathscr{E}°(\text{anode}) = 0.800 - 0.000\ \mathrm{V} = 0.800\ \mathrm{V}$$

Note that $n = 2$ for the overall cell reaction, and the reaction quotient simplifies to

$$Q = \frac{[\mathrm{H_3O^+}]^2}{[\mathrm{Ag^+}]^2\, P_{\mathrm{H_2}}} = \frac{1}{[\mathrm{Ag^+}]^2}$$

because $[H_3O^+] = 1$ M and $P_{H_2} = 1$ atm. The Nernst equation is

$$\Delta\mathscr{E} = \Delta\mathscr{E}° - \frac{0.0592\ \mathrm{V}}{n}\log_{10} Q$$

$$\log_{10} Q = \frac{n}{0.0592\ \mathrm{V}}(\Delta\mathscr{E}° - \Delta\mathscr{E}) = \frac{2}{0.0592\ \mathrm{V}}(0.800\ \mathrm{V} - 0.397\ \mathrm{V}) = 13.6$$

$$Q = 10^{13.6} = 4 \times 10^{13} = 1/[\mathrm{Ag^+}]^2$$

This can be solved for the silver ion concentration $[Ag^+]$ to give

$$[\mathrm{Ag^+}] = 1.6 \times 10^{-7}\ \mathrm{M}$$

so that

$$[\mathrm{Ag^+}][\mathrm{Cl^-}] = (1.6 \times 10^{-7})(1.00 \times 10^{-3})$$

$$K_{sp} = 1.6 \times 10^{-10}$$

Related Problems: 41, 42

pH Meters

The voltage of a galvanic cell is sensitive to the pH if one of its electrodes is a $Pt|H_2$ electrode that dips into a solution of variable pH. A simple cell to measure pH is

$$\mathrm{Pt}|\mathrm{H_2}(1\ \mathrm{atm})|\mathrm{H_3O^+}(\text{variable})\ ||\ \mathrm{H_3O^+}(1\ \mathrm{M})|\mathrm{H_2}(1\ \mathrm{atm})|\mathrm{Pt}$$

If the half-cell reactions are written as

$$\mathrm{H_2}(1\ \mathrm{atm}) + 2\ \mathrm{H_2O}(\ell) \longrightarrow 2\ \mathrm{H_3O^+}(\text{var}) + 2\ e^- \qquad \text{(anode)}$$

$$2\ \mathrm{H_3O^+}(1\ \mathrm{M}) + 2\ e^- \longrightarrow \mathrm{H_2}(1\ \mathrm{atm}) + 2\ \mathrm{H_2O}(\ell) \qquad \text{(cathode)}$$

then $n = 2$ and $Q = [H_3O^+(\text{variable})]^2$ because the other concentrations and gas pressures are 1 M and 1 atm, respectively. From the Nernst equation,

$$\Delta\mathscr{E} = \Delta\mathscr{E}° - \frac{0.0592\ \mathrm{V}}{n}\log_{10} Q$$

and because $\Delta\mathcal{E}° = 0$,

$$\Delta\mathcal{E} = -\frac{0.0592\text{ V}}{2}\log_{10}[\text{H}_3\text{O}^+]^2$$

$$= -0.0592\text{ V}\log_{10}[\text{H}_3\text{O}^+] = (0.0592\text{ V})\text{ pH}$$

The measured cell voltage is proportional to the pH.

We have just described a simple **pH meter.** Because it is inconvenient to have to bubble hydrogen gas through the unknown and reference half-cells, a more portable and miniaturized pair of electrodes is used to replace the hydrogen half-cells. In a typical commercial pH meter, two electrodes are dipped into the solution of unknown pH. One of these, the **glass electrode,** usually consists of an AgCl-coated silver electrode in contact with an HCl solution of known (e.g., 1.0 M) concentration in a thin-walled glass bulb. A pH-dependent potential develops across this thin glass membrane when the glass electrode is immersed in a solution of different, unknown $[\text{H}_3\text{O}^+]$. The second half-cell is often a **saturated calomel electrode,** consisting of a platinum wire in electrical contact with a paste of liquid mercury, calomel ($\text{Hg}_2\text{Cl}_2(s)$), and a saturated solution of KCl. The overall cell (Fig. 17.5) can be represented as

$$\text{Ag}|\text{AgCl}|\text{Cl}^- + \text{H}_3\text{O}^+(1.0\text{ M})|\text{glass}|\text{H}_3\text{O}^+(\text{var})||\text{Cl}^-(\text{sat})|\text{Hg}_2\text{Cl}_2(s)|\text{Hg}|\text{Pt}$$

whose half-reactions are

$$2\text{Ag}(s) + 2\text{Cl}^-(1.0\text{ M}) \longrightarrow 2\text{AgCl}(s) + 2e^- \qquad \text{(anode)}$$

$$\text{H}_3\text{O}^+(1.0\text{ M}) \longrightarrow \text{H}_3\text{O}^+(\text{var})$$

$$\text{Hg}_2\text{Cl}_2(s) + 2\,e^- \longrightarrow 2\text{Hg}(\ell) + 2\text{Cl}^-(\text{sat}) \qquad \text{(cathode)}$$

The first and third half-reactions have half-cell potentials $\mathcal{E}(\text{AgCl}|\text{Cl}^+|\text{Ag})$ and $\mathcal{E}(\text{Hg}_2\text{Cl}_2|\text{Cl}^+|\text{Hg})$ that can be combined and called $\Delta\mathcal{E}_{\text{ref}}$ because they make a constant contribution to the cell voltage. The second reaction is the source of a variable potential in the cell, corresponding to the free energy of dilution of H_3O^+ from a concentration of 1.0 M to an unknown and variable concentration, and its potential exists across the thin glass membrane of the glass electrode. The Nernst equation for the cell can therefore be written as

$$\Delta\mathcal{E} = \Delta\mathcal{E}(\text{ref}) - \frac{0.0592\text{ V}}{1}\log_{10}\frac{[\text{H}_3\text{O}^+(\text{var})]}{1.00}$$

$$= \Delta\mathcal{E}(\text{ref}) + (0.0592\text{V})\text{ pH}$$

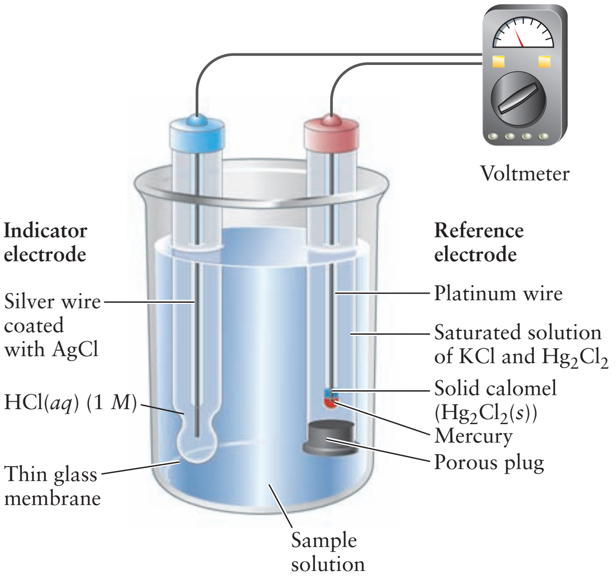


FIGURE 17.5 A pH meter consists of a glass electrode (left) and a calomel electrode (right), both of which dip into a solution of unknown hydronium ion concentration.

and the pH of the unknown solution is

$$\mathrm{pH} = \frac{\Delta\mathscr{E} - \Delta\mathscr{E}(\mathrm{ref})}{0.0592\mathrm{V}}$$

The glass electrode has a number of advantages. It responds only to changes in $[H_3O^+]$ and does so over a wide range of pH. It is unaffected by strong oxidizing agents that would make a hydrogen electrode unreliable. Highly colored solutions that would render acid–base indicators useless do not interfere with the glass electrode. Finally, the glass electrode can be miniaturized to permit insertion into individual living cells and therefore finds wide use in biology.

Other types of electrodes have been designed to measure the concentrations of ions other than H_3O^+. The simplest example of such an **ion-selective electrode** is a metal wire, which can be used to detect the concentration of the corresponding metal ion in solution. Silver and copper wires can be used reproducibly in this way to determine the concentrations of Ag^+ and Cu^{2+}, respectively. Still other electrodes have been developed to detect specific ions. For example, glasses of chemically modified composition are used to construct membrane electrodes to determine potassium and sodium ions or halogen ions.

17.4 Batteries and Fuel Cells

The electrochemistry of galvanic cells leads to a variety of applications in industry and in everyday life. This section focuses on two of the most important: batteries to store energy and fuel cells to convert chemical energy to electrical energy.

Batteries

The origin of the **battery** is lost in history, but it is believed that Persian artisans must have used some form of battery to gold-plate jewelry as long ago as the second century B.C. The modern development of the battery began with Alessandro Volta in 1800. Volta constructed a stack of alternating zinc and silver disks, between pairs of which were inserted disks of paper saturated with a salt solution. This device generated a potential difference across its ends that could cause electrical shock if the stack contained enough disks. In Volta's invention, a large number of galvanic cells were arranged in series (cathode to anode) so that their individual voltages added together. Such an arrangement is, strictly speaking, a **battery of cells,** but modern usage makes no distinction between a single cell and a voltaic pile, and the word *battery* has come to mean the cell itself. Cells that are discarded when their electrical energy has been spent are called **primary** cells, and those that can be recharged are **secondary** cells.

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Batteries vary in size and chemistry. Shown here are an automobile lead-storage battery, rechargeable nickel–cadmium cells, alkaline cells, and zinc–carbon dry cells.

The most familiar primary cell is the **Leclanché cell** (also called a *zinc–carbon dry cell*) used for flashlights, portable radios, and a host of other purposes. Each year, more than 5 billion such dry cells are used worldwide, and estimates place the quantity of zinc consumed for this purpose at more than 30 metric tons per day. The "dry cell" is not really dry at all. Rather, its electrolyte is a moist powder containing ammonium chloride and zinc chloride. Figure 17.6 is a cutaway illustration of a dry cell, which consists of a zinc shell for an anode (negative pole) and an axial graphite rod for a cathode (positive pole), with the rod surrounded by a densely packed layer of graphite and manganese dioxide. Each of these components performs an interesting and essential function. At the zinc anode, oxidation takes place:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^- \text{ (anode)}$$

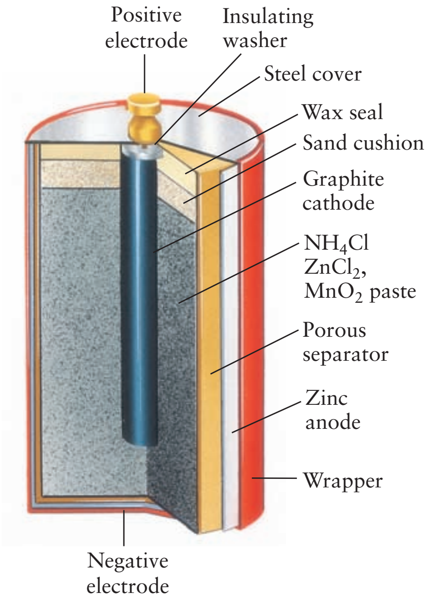

FIGURE 17.6 In a Leclanché dry cell, electrons are released to an external circuit at the anode and enter the cell again at the cathode, where the reduction of MnO_2 occurs.

The moist salt mixture permits ions to transport through the cell a net charge equal to that carried by electrons in the external circuit, just as a salt bridge does in the cells we have considered until now. Manganese dioxide is the ultimate electron acceptor and is reduced to Mn_2O_3 by electrons that pass to it from the graphite rod through the graphite particles:

$$2\ MnO_2(s) + 2\ NH_4^+(aq) + 2\ e^- \longrightarrow Mn_2O_3(s) + 2\ NH_3(aq) + H_2O(\ell) \quad \text{(cathode)}$$

The ingenious procedure of mixing powdered graphite with powdered MnO_2 greatly increases the effective surface area of the cathode, reduces the internal resistance of the cell, and enables currents of several amperes to flow. The overall cell reaction is

$$Zn(s) + 2\ MnO_2(s) + 2\ NH_4^+(aq) \longrightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2\ NH_3(aq) + H_2O(\ell)$$

The cell components are hermetically sealed in a steel shell that is in contact with the zinc and acts as the negative terminal of the battery. A fresh zinc–carbon dry cell generates a potential difference of 1.5 V.

The Leclanché cell has the disadvantage that its concentrations change with time, and thus the voltage of the battery falls as it is used. In an **alkaline dry cell,** the ammonium chloride is replaced by potassium hydroxide, and the half-cell reactions become

$$Zn(s) + 2\ OH^-(aq) \longrightarrow Zn(OH)_2(s) + 2\ e^- \quad \text{(anode)}$$

$$2\ MnO_2(s) + H_2O(\ell) + 2\ e^- \longrightarrow Mn_2O_3(s) + 2\ OH^-(aq) \quad \text{(cathode)}$$

The overall reaction is then

$$Zn(s) + 2\ MnO_2(s) + H_2O(\ell) \longrightarrow Zn(OH)_2(s) + Mn_2O_3(s)$$

Because dissolved species do not appear in the overall reaction, concentrations do not change significantly and a steadier voltage results.

A third primary dry cell is the **zinc–mercuric oxide cell** depicted in Figure 17.7. It is commonly given the shape of a small button and is used in automatic cameras, hearing aids, digital calculators, and quartz–electric watches. This battery has an anode that is a mixture of mercury and zinc and a steel cathode in contact with solid mercury(II) oxide (HgO). The electrolyte is a 45% KOH solution that saturates an absorbent material. The anode half-reaction is the same as that in an alkaline dry cell,

$$Zn(s) + 2\ OH^-(aq) \longrightarrow Zn(OH)_2(s) + 2\ e^- \quad \text{(anode)}$$

but the cathode half-reaction is now

$$HgO(s) + H_2O(\ell) + 2\ e^- \longrightarrow Hg(\ell) + 2\ OH^-(aq) \quad \text{(cathode)}$$

The overall reaction is

$$Zn(s) + HgO(s) + H_2O(\ell) \longrightarrow Zn(OH)_2(s) + Hg(\ell)$$

This cell has a very stable output of 1.34 V, a fact that makes it especially valuable for use in communication equipment and scientific instruments.

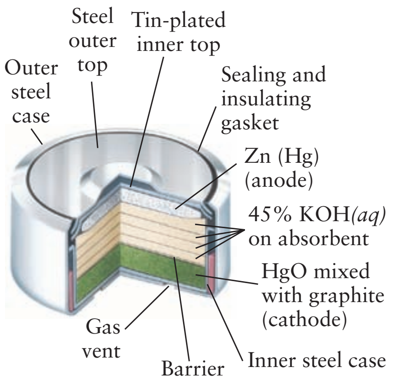

FIGURE 17.7 A zinc–mercuric oxide dry cell, used in electric watches and cameras.

Rechargeable Batteries

In some batteries the electrodes can be regenerated after depletion by imposing an external potential across them that reverses the direction of current flow through the cell. These are called **secondary batteries,** and the process of reconstituting them to their original state is called "recharging." To recharge a run-down secondary battery, the voltage of the external source must be larger than that of the battery in its original state and, of course, opposite in polarity.

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FIGURE 17.8 Rechargeable nickel–cadmium batteries.

The **nickel–cadmium cell** (or *nicad battery;* Fig. 17.8) is used in handheld electronic calculators and other cordless electric implements such as portable shavers. Its half-cell reactions during discharge are

$$\begin{array}{rl}
Cd(s) + 2\ OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2\ e^- & \text{(anode)} \\
2\ NiO(OH)(s) + 2\ H_2O(\ell) + 2\ e^- \longrightarrow 2\ Ni(OH)_2(s) + 2\ OH^-(aq) & \text{(cathode)} \\
\hline
Cd(s) + 2\ NiO(OH)(s) + 2\ H_2O(\ell) \longrightarrow Cd(OH)_2(s) + 2\ Ni(OH)_2(s) &
\end{array}$$

This battery gives a fairly constant voltage of 1.4 V. When it is connected to an external voltage source, the preceding reactions are reversed as the battery is recharged.

One technically important secondary battery is the **lead–acid storage battery,** used in automobiles. A 12-V lead storage battery consists of six 2.0-V cells (Fig. 17.9) connected in series (cathode to anode) by an internal lead linkage and housed in a hard rubber or plastic case. In each cell the anode consists of metallic lead in porous form to maximize its contact area with the electrolyte. The cathode is of similar design, but its lead has been converted to lead dioxide. A sulfuric acid solution (37% by mass) serves as the electrolyte.

When the external circuit is completed, electrons are released from the anode to the external circuit and the resulting Pb^{2+} ions precipitate on the electrode as insoluble lead sulfate. At the cathode, electrons from the external circuit reduce PbO_2 to water and Pb^{2+} ions, which also precipitate as $PbSO_4$ on that electrode. The half-cell reactions are

$$\begin{array}{rl}
Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2\ e^- & \text{(anode)} \\
PbO_2(s) + SO_4^{2-}(aq) + 4\ H_3O^+(aq) + 2\ e^- \longrightarrow PbSO_4(s) + 6\ H_2O(\ell) & \text{(cathode)} \\
\hline
Pb(s) + PbO_2(s) + 2\ SO_4^{2-}(aq) + 4\ H_3O^+(aq) \longrightarrow 2\ PbSO_4(s) + 6\ H_2O(\ell) &
\end{array}$$

The anode and cathode are both largely converted to $PbSO_4(s)$ when the storage battery is fully discharged, and because sulfuric acid is a reactant, its concentration falls. Measuring the density of the electrolyte provides a quick way to estimate the state of charge of the battery.

When a voltage in excess of 12 V is applied across the terminals of the battery in the opposite direction, the half-cell reactions are reversed. This part of the cycle restores the battery to its initial state, ready to be used in another work-producing discharge half-cycle. Lead–acid storage batteries endure many thousands of cycles of discharge and charge before they ultimately fail because of the flaking off of $PbSO_4$ from the electrodes or the development of internal short circuits. In automobiles they are usually not designed to undergo complete discharge–recharge cycles. Instead, a generator converts some of the kinetic energy of the vehicle to electrical energy for continuous or intermittent charging. About 1.8×10^7 J can be obtained in the discharge of an average automobile battery, and currents as large as 100 A are drawn for the short time needed to start the engine.

A drawback of the lead–acid storage battery is its low energy density, the amount of energy obtainable per kilogram of battery mass. This is not important when a battery is used to start a gasoline-powered automobile, but it precludes the battery's use in a vehicle driven by an electric motor. This difficulty of a low energy-to-mass ratio, which limits the range of vehicle operation before recharge is necessary, has spurred electrochemists to develop secondary batteries that have much higher energy densities.

One promising line of approach has been the development of rechargeable batteries that use an alkali metal (lithium or sodium) as the anode and sulfur as the electron acceptor. Sulfur is a nonconductor of electricity, so graphite is used as the cathode that conducts electrons to it. The elements must be in their liquid states, so these batteries are high-temperature cells (sulfur melts at 112°C, lithium at

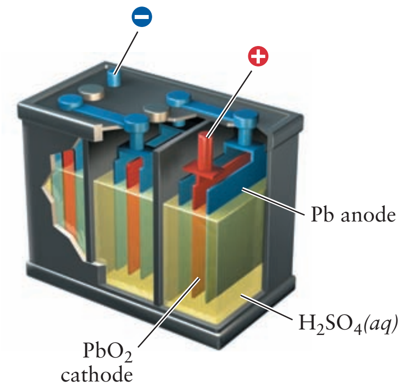

FIGURE 17.9 In a lead–acid storage battery, anodes made of Pb alternate with cathodes of Pb coated with PbO_2. The electrolyte is sulfuric acid.

186°C, and sodium at 98°C). The sodium–sulfur cell (Fig. 17.10), for example, has an optimal operating temperature of 250°C. The half-cell reactions are

$$\begin{array}{ll} 2\ \mathrm{Na} \rightarrow 2\ \mathrm{Na}^+ + 2\ e^- & \text{(anode)} \\ \mathrm{S} + 2\ e^- \rightarrow \mathrm{S}^{2-} & \text{(cathode)} \\ \hline 2\ \mathrm{Na} + \mathrm{S} \rightarrow 2\ \mathrm{Na}^+ + \mathrm{S}^{2-} & \end{array}$$

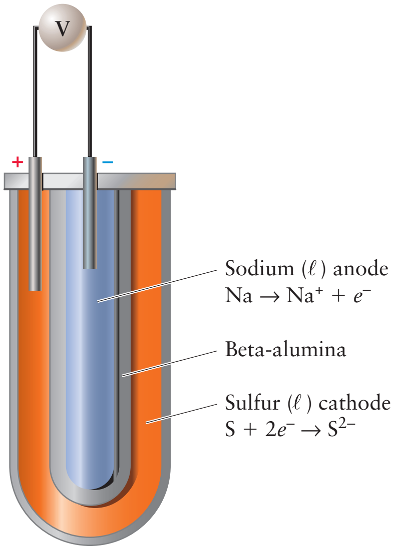

FIGURE 17.10 In a sodium–sulfur battery, Na^+ ions migrate through beta-alumina to the cathode to equalize the charge as electrons flow spontaneously from the anode to the cathode through the external circuit.

This is actually an oversimplification of the cathodic process because sulfide ion forms polysulfides with sulfur:

$$S^{2-} + nS \longrightarrow S_{n+1}^{2-}$$

but the fundamental principles of the cell operation are the same.

What makes the sodium–sulfur cell possible is a remarkable property of a compound called beta-alumina, which has the composition $NaAl_{11}O_{17}$. Beta-alumina allows sodium ions to migrate through its structure very easily, but it blocks the passage of polysulfide ions. Therefore, it can function as a semipermeable medium like the membranes used in osmosis (see Section 11.5). Such an ion-conducting solid electrolyte is essential to prevent direct chemical reaction between sulfur and sodium. The lithium–sulfur battery operates on similar principles, and other solid electrolytes such as calcium fluoride, which permits ionic transport of fluoride ion, may find use in cells based on those elements.

The considerable promise of the alkali metal–sulfur cell lies in its high energy density, which makes it possible to construct lightweight batteries capable of generating large currents. Their use in electric cars is an attractive possibility. As the cost of petroleum-based fuels increases and their supply becomes less reliable, cells such as the alkali metal–sulfur battery may come into practical applications.

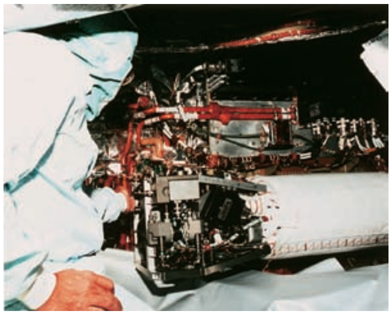
NASA

FIGURE 17.11 A hydrogen–oxygen fuel cell used on U.S. space missions.

Fuel Cells

A battery is a closed system that delivers electrical energy by electrochemical reactions. Once the chemicals originally present are consumed, the battery must be either recharged or discarded. In contrast, a **fuel cell** is designed for continuous operation, with reactants (fuel) being supplied and products removed continuously. It is an energy converter, transforming chemical energy into electrical energy. Fuel cells based on the reaction

$$2\ H_2(g) + O_2(g) \longrightarrow 2\ H_2O(\ell)$$

were used on the Gemini and Apollo space vehicles to help meet the electrical requirements of the missions (Fig. 17.11). After the product was purified by ion exchange, the crew consumed it as drinking water.

Figure 17.12 represents the hydrogen–oxygen fuel cell schematically. The electrodes can be any nonreactive conductor (graphite, for example); their function is to conduct electrons into and out of the cell and to facilitate electron exchange between the gases and the ions in solution. The electrolyte transports charge through the cell, and the ions dissolved in it participate in the half-reactions at each electrode. Acidic solutions present corrosion problems, so an alkaline solution is preferable (1 M NaOH, for instance). The anode half-reaction is then

$$H_2(g) + 2\ OH^-(aq) \longrightarrow 2\ H_2O(\ell) + 2\ e^-$$

and the cathode reaction is

$$\tfrac{1}{2}\ O_2(g) + H_2O(\ell) + 2\ e^- \longrightarrow 2\ OH^-(aq)$$

The standard reduction potentials at 25°C (1 M concentrations, 1 atm pressure) are

$$\mathscr{E}°\ (H_2|H_2O) = -0.828\ \text{V} \quad \text{and} \quad \mathscr{E}°\ (O_2|OH^-) = 0.401\ \text{V}$$

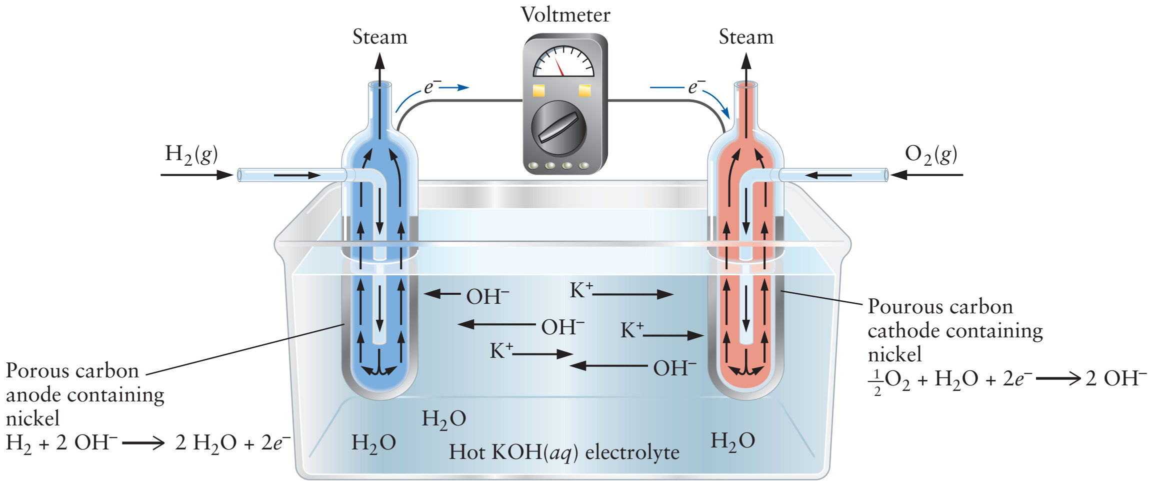

FIGURE 17.12 In a hydrogen–oxygen fuel cell, the two gases are fed in separately and are oxidized or reduced on the electrodes. A hot solution of potassium hydroxide between the electrodes completes the circuit, and the steam produced in the reaction evaporates from the cell continuously.

The overall cell reaction is the production of water,

$$H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow H_2O(\ell)$$

and the cell voltage is

$$\Delta\mathscr{E}° = \mathscr{E}°\,(\text{cathode}) - \mathscr{E}°\,(\text{anode}) = 0.401 - (-0.828) = 1.229\text{ V}$$

The overall cell voltage does not depend on pH because the OH^- has dropped out; the same voltage would be obtained in an acidic fuel cell.

Another practical fuel cell accomplishes the overall reaction

$$CO(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow CO_2(g)$$

for which the half-reactions are

$$CO(g) + 3\,H_2O(\ell) \longrightarrow CO_2(g) + 2\,H_3O^+(aq) + 2\,e^- \qquad \text{(anode)}$$

$$\tfrac{1}{2}\,O_2(g) + 2\,H_3O^+(aq) + 2\,e^- \longrightarrow 3\,H_2O(\ell) \qquad \text{(cathode)}$$

The electrolyte is usually concentrated phosphoric acid, and the operating temperature is between 100°C and 200°C. Platinum is the electrode material of choice because it facilitates the electron transfer reactions.

Natural gas (largely CH_4) and even fuel oil can be "burned" electrochemically to provide electrical energy by either of two approaches. They can be converted to CO and H_2 or to CO_2 and H_2 before use in a fuel cell by reaction with steam,

$$CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3\,H_2(g)$$

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

at temperatures of about 500°C. Alternatively, they can be used directly in a fuel cell at higher temperatures (up to 750°C) with a molten alkali metal carbonate as the electrolyte. Either type of fuel cell is attractive as an electrochemical energy converter in regions where hydrocarbon fuels are readily available but large-scale power plants (fossil or nuclear) are remote.

The theoretical advantage of electrochemical fuel cells over more traditional fuel technology can be seen from a thermodynamic analysis. If a chemical reaction such as the oxidation of a fuel can be carried out electrochemically, the maximum (reversible) work obtainable is equal to the free energy change ΔG (see Section 17.2):

$$+w_{\text{max}}(\text{fuel cell}) = |\Delta G|$$

In traditional fuel technology, the same fuel would be burned in air, producing an amount of heat $q_P = \Delta H$, the enthalpy of combustion. The heat would then be used to run a heat engine-generator system to produce electrical power. The efficiency of conversion of heat to work is limited by the laws of thermodynamics. If the heat is supplied at temperature T_h and if the lower operating temperature is T_l, the maximum work obtainable (see Section 13.4) is

$$-w_{\text{max}}(\text{heat engine}) = \epsilon|q_P| = \frac{T_h - T_l}{T_h}|\Delta H|$$

Because the magnitude of ΔH is generally comparable to that of ΔG for fuel oxidation reactions, the fuel cell will be more efficient because the factor $(T_h - T_l)/T_h$ for a thermal engine is much less than 1. In practice, fuel cells and heat engines must be operated irreversibly (to increase the rate of energy production), and the work obtained with both is less than w_{max}. The overall efficiency of practical heat engines rarely exceeds 30% to 35%, whereas that of fuel cells can be in the 60% to 70% range. This advantage of fuel cell technology is partially offset by the greater expense of constructing and maintaining fuel cells, however.

17.5 Corrosion and Its Prevention

The **corrosion** of metals is one of the most significant problems faced by advanced industrial societies (Fig. 17.13). It has been estimated that in the United States alone, the annual cost of corrosion amounts to tens of *billions* of dollars. Effects of corrosion are both visible (the formation of rust on exposed iron surfaces) and invisible (the cracking and resulting loss of strength of metal beneath the surface). The mechanism of corrosion must be understood before processes can be developed for its prevention.

Although corrosion is a serious problem for many metals, we will focus on the spontaneous electrochemical reactions of iron. Corrosion can be pictured as a "short-circuited" galvanic cell, in which some regions of the metal surface act as cathodes and others as anodes, and the electric "circuit" is completed by electron flow through the iron itself. These electrochemical cells form in parts of the metal where there are impurities or in regions that are subject to stress. The anode reaction is

$$\text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2\,e^-$$

Various cathode reactions are possible. In the absence of oxygen (for example, at the bottom of a lake), the corrosion reactions are

$$\begin{array}{ll} \text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2\,e^- & \text{(anode)} \\ \underline{2\,\text{H}_2\text{O}(\ell) + 2\,e^- \longrightarrow 2\,\text{OH}^-(aq) + \text{H}_2(g)} & \text{(cathode)} \\ \text{Fe}(s) + 2\,\text{H}_2\text{O}(\ell) \longrightarrow \text{Fe}^{2+}(aq) + 2\,\text{OH}^-(aq) + \text{H}_2(g) & \end{array}$$

These reactions are generally slow and do not cause serious amounts of corrosion. Far more extensive corrosion takes place when the iron is in contact with both oxygen and water. In this case the cathode reaction is

$$\tfrac{1}{2}\,\text{O}_2(g) + 2\,\text{H}_3\text{O}^+(aq) + 2\,e^- \longrightarrow 3\,\text{H}_2\text{O}(\ell)$$

The Fe^{2+} ions formed simultaneously at the anode migrate to the cathode, where they are further oxidized by O_2 to the +3 oxidation state to form rust ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$), a hydrated form of iron(III) oxide:

$$2\,\text{Fe}^{2+}(aq) + \tfrac{1}{2}\,\text{O}_2(g) + (6 + x)\text{H}_2\text{O}(\ell) \longrightarrow \text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O} + 4\,\text{H}_3\text{O}^+(aq)$$

The hydronium ions produced in this reaction allow the corrosion cycle to continue.


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FIGURE 17.13 Rust.

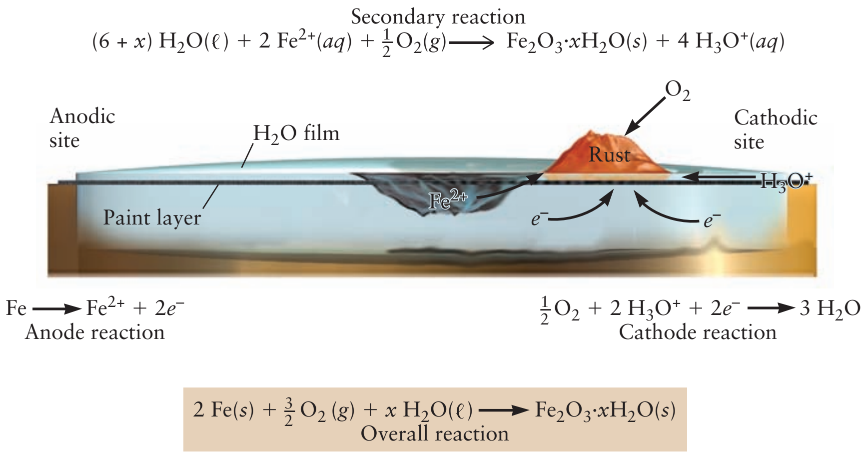

FIGURE 17.14 The corrosion of iron. Note that pitting occurs in the anodic region, and rust appears in the cathodic region.

When a portion of the paint that protects a piece of iron or steel is chipped off (Fig. 17.14), the exposed area acts as the cathode because it is open to the atmosphere (air and water) and is therefore rich in oxygen, whereas oxygen-poor areas *under* the paint act as anodes. Rust forms on the cathode (the visible, exposed region), and pitting (loss of metal through oxidation of iron and flow of metal ions to the cathode) occurs at the anode. This pitting can lead to loss of structural strength in girders and other supports. The most serious harm done by corrosion is not the visible rusting but the damage done beneath the painted surface.

A number of factors speed corrosion. Dissolved salt provides an electrolyte that improves the flow of charge through solution; a well-known example is the rapid rusting of cars in areas where salt is spread on icy roads. Higher acidity also increases corrosion, as seen by the role of H_3O^+ as a reactant in the reduction process at the cathode. Acidity is enhanced by the presence of dissolved CO_2 (which produces H_3O^+ and HCO_3^- ions) and by air pollution from oxides of sulfur, which leads to the formation of dissolved sulfuric acid in acid precipitation.

Corrosion of iron can be inhibited in a number of ways. Coatings of paint or plastics obviously protect the metal, but they can crack or suffer other damage, thereby localizing and accentuating the process. An important method of protecting metals arises from the phenomenon of **passivation,** in which a thin metal oxide layer forms on the surface and prevents further electrochemical reactions. Some metals become passivated spontaneously upon exposure to air; aluminum, for example, reacts with oxygen to form a thin protective layer of Al_2O_3. Special paints designed to prevent rusting contain potassium dichromate ($K_2Cr_2O_7$) and lead oxide (Pb_3O_4), which cause the superficial oxidation and passivation of iron. Stainless steel is an alloy of iron with chromium in which the chromium leads to passivation and prevents rusting.

A different way of preventing iron corrosion is to use a **sacrificial anode.** A comparison of the standard reduction potentials of iron and magnesium

$$Fe^{2+} + 2\ e^- \longrightarrow Fe(s) \qquad \mathscr{E}° = -0.41\ V$$

$$Mg^{2+} + 2\ e^- \longrightarrow Mg(s) \qquad \mathscr{E}° = -2.39\ V$$

shows that Mg^{2+} is much harder to reduce than Fe^{2+} or, conversely, that Mg(*s*) is more easily oxidized than Fe(*s*). A piece of magnesium in electrical contact with iron is oxidized in preference to the iron, and the iron is therefore protected. The magnesium is the sacrificial anode, and once it is consumed by oxidation it must be replaced. This method is used to protect ship hulls, bridges, and iron water pipes from corrosion. Magnesium plates are attached at regular intervals along a piece of buried pipe, and it is far easier to replace them periodically than to replace the entire pipe.

17.6 Electrometallurgy


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FIGURE 17.15 A specimen of native copper.

The recovery of metals from their sources in the earth is the science of **extractive metallurgy,** a discipline that draws on chemistry, physics, and engineering for its methods. As a science it is a comparatively recent subject, but its beginnings, which were evidently in the Near East about 6000 years ago, marked the emergence of humanity from the Stone Age. The earliest known metals were undoubtedly gold, silver, and copper because they could be found in their native (elemental) states (Fig. 17.15). Gold and silver were valued for their ornamental uses, but they are too soft to have been made into tools. Iron was also found in elemental form—although rarely—in meteorites.

Most metals in nature are combined with other elements such as oxygen and sulfur in ores, and chemical processes are required to free them. As Table 17.1 shows, the free energies of formation of most metal oxides are negative, indicating that the reverse reactions, which would yield the free metal and oxygen, have positive free energy changes. Scientists can carry out one of these reverse reactions to obtain the free metal only by coupling it with a second, spontaneous chemical reaction. The greater the cost in free energy, the more difficult the production of the free metal. Thus, silver and gold (at the bottom of Table 17.1) exist in nature as elements, and mercury can be released from its oxide or sulfide ore (cinnabar) merely by moderate heating (see Fig. 1.6). Extracting pure copper, zinc, and iron requires more stringent conditions; the ores of these metals are reduced in chemical reactions at high temperatures, collectively called **pyrometallurgy.** These reactions are carried out in huge furnaces, in which a fuel such as coke (coal from which volatile components have been expelled) serves both as the reducing agent and as the source of heat to maintain the required high temperatures. The process, called **smelting,** involves both chemical change and melting. The combustion of carbon

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta G° = -394 \text{ kJ mol}^{-1}$$

provides the driving force for the overall reaction.

TABLE 17.1 Metal Oxides Arranged According to Ease of Reduction

Metal Oxide	Metal	n[†]	$\Delta G_f°/n$[†] (kJ mol^{-1})	A Method of Production of the Metal
MgO	Mg	2	−285	Electrolysis of $MgCl_2$
Al_2O_3	Al	6	−264	Electrolysis
TiO_2	Ti	4	−222	Reaction with Mg
Na_2O	Na	2	−188	Electrolysis of NaCl
Cr_2O_3	Cr	6	−176	Electrolysis, reduction by Al
ZnO	Zn	2	−159	Smelting of ZnS
SnO_2	Sn	4	−130	Smelting
Fe_2O_3	Fe	6	−124	Smelting
NiO	Ni	2	−106	Smelting of nickel sulfides
PbO	Pb	2	−94	Smelting of PbS
CuO	Cu	2	−65	Smelting of $CuFeS_2$
HgO	Hg	2	−29	Moderate heating of HgS
Ag_2O	Ag	2	−6	Found in elemental form
Au_2O_3	Au	6	>0	Found in elemental form

[†] The standard free energies of formation of the metal oxides in kJ mol^{-1} are adjusted for fair comparison by dividing them by n, the total decrease in oxidation state required to reduce the metal atoms contained in the oxide to oxidation states of 0. Thus, the reduction of Cr_2O_3 involves a change in the oxidation state of two chromium atoms from +3 to 0, so $n = 2 \times 3 = 6$.

Even smelting is not sufficient to recover the metals at the top of Table 17.1, which have the most negative free energies of formation for their oxides (and for their sulfides as well). These metals have particularly high values of free energy relative to their compounds found in readily available ores. **Electrometallurgy,** or electrolytic production, provides the best ways of recovering such elements from their ores. Electrochemical cells are also used to purify the metals produced by the techniques of pyrometallurgy.

Aluminum

Aluminum is the third most abundant element in the earth's crust (after oxygen and silicon), accounting for 8.2% of the total mass. It occurs most commonly in association with silicon in the aluminosilicates of feldspars and micas and in clays, the products of weathering of these rocks. The most important ore for aluminum production is bauxite, a hydrated aluminum oxide that contains 50% to 60% Al_2O_3; 1% to 20% Fe_2O_3; 1% to 10% silica; minor concentrations of titanium, zirconium, vanadium, and other transition-metal oxides; and the balance (20% to 30%) water. Bauxite is purified via the **Bayer process,** which takes advantage of the fact that the amphoteric oxide alumina is soluble in strong bases but iron(III) oxide is not. Crude bauxite is dissolved in sodium hydroxide

$$\mathrm{Al_2O_3}(s) + 2\ \mathrm{OH^-}(aq) + 3\ \mathrm{H_2O}(\ell) \longrightarrow 2\ \mathrm{Al(OH)_4^-}(aq)$$

and separated from hydrated iron oxide and other insoluble impurities by filtration. Pure hydrated aluminum oxide precipitates when the solution is cooled to supersaturation and seeded with crystals of the product:

$$2\ \mathrm{Al(OH)_4^-}(aq) \longrightarrow \mathrm{Al_2O_3{\cdot}3H_2O}(s) + 2\ \mathrm{OH^-}(aq)$$

The water of hydration is removed by calcining at high temperature (1200°C).

Compared with copper, iron, gold, and lead, which were known in antiquity, aluminum is a relative newcomer. Sir Humphry Davy obtained it as an alloy of iron and proved its metallic nature in 1809. It was first prepared in relatively pure form in 1825 by H. C. Oersted through reduction of aluminum chloride with an amalgam of potassium dissolved in mercury,

$$\mathrm{AlCl_3}(s) + 3\ \mathrm{K(Hg)}_x(\ell) \longrightarrow 3\ \mathrm{KCl}(s) + \mathrm{Al(Hg)}_{3x}(\ell)$$

after which the mercury was removed by distillation. Aluminum remained largely a laboratory curiosity until 1886, when Charles Hall in the United States (then a 21-year-old graduate of Oberlin College) and Paul Héroult (a Frenchman of the same age) independently invented an efficient process for its production. In the 1990s the worldwide production of aluminum by the **Hall–Héroult process** was approximately 1.5×10^7 metric tons per year.

The Hall–Héroult process involves the cathodic deposition of aluminum, from molten cryolite (Na_3AlF_6) containing dissolved Al_2O_3, in electrolysis cells (Fig. 17.16). Each cell consists of a rectangular steel box some 6 m long, 2 m wide, and 1 m high, which serves as the cathode, and massive graphite anodes that extend through the roof of the cell into the molten cryolite bath. Enormous currents (50,000 to 100,000 A) are passed through the cell, and as many as 100 such cells may be connected in series.

Molten cryolite, which is completely dissociated into Na^+ and AlF_6^{3-} ions, is an excellent solvent for aluminum oxide, giving rise to an equilibrium distribution of ions such as Al^{3+}, AlF^{2+}, AlF_2^+, . . . , AlF_6^{3-}, and O^{2-} in the electrolyte. Cryolite melts at 1000°C, but its melting point is lowered by dissolved aluminum oxide, so the operating temperature of the cell is about 950°C. Compared with the melting point of pure Al_2O_3 (2050°C), this is a low temperature, and it is the reason the Hall–Héroult process has succeeded. Molten aluminum is somewhat denser than the melt at 950°C and therefore collects at the bottom of the cell, from which it is

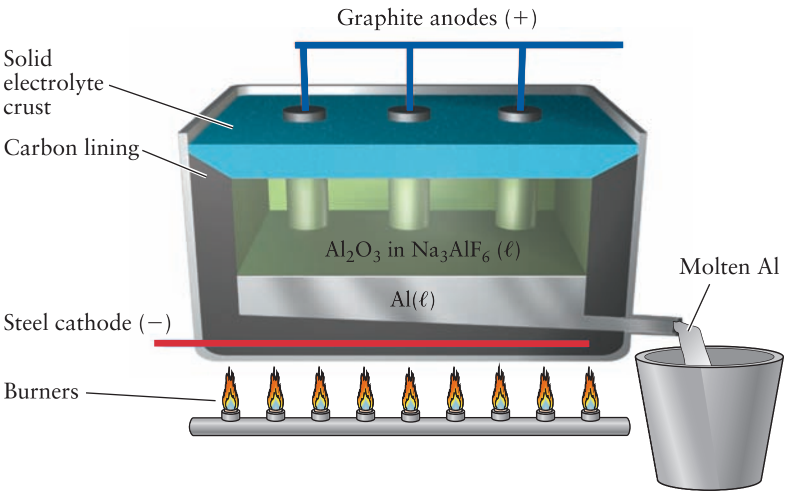


FIGURE 17.16 An electrolytic cell used in the Hall–Héroult process for production of aluminum.

tapped periodically. Oxygen is the primary anode product, but it reacts with the graphite electrode to produce carbon dioxide. The overall cell reaction is

$$2\ Al_2O_3 + 3\ C \longrightarrow 4\ Al + 3\ CO_2$$

Aluminum and its alloys have a tremendous variety of applications. Many of these make use of aluminum's low density (Table 17.2), an advantage over iron or steel when weight savings are desirable—such as in the transportation industry, which uses aluminum in vehicles from automobiles to satellites. Aluminum's high electrical conductivity and low density make it useful for electrical transmission lines. For structural and building applications, its resistance to corrosion is an important feature, as is the fact that it becomes stronger at subzero temperatures. (Steel and iron sometimes become brittle under these circumstances.) Household products that contain aluminum include foil, soft drink cans, and cooking utensils.

TABLE 17.2 Densities of Selected Metals

Metal	Density (g cm^{-3}) at Room Conditions
Li	0.534
Na	0.971
Mg	1.738
Al	2.702
Ti	4.54
Zn	7.133
Fe	7.874
Ni	8.902
Cu	8.96
Ag	10.500
Pb	11.35
U	18.95
Au	19.32
Pt	21.45

Magnesium

Like aluminum, magnesium is an abundant element on the surface of the earth, but it is not easy to prepare in elemental form. Although ores such as dolomite ($CaMg(CO_3)_2$) and carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) exist, the major commercial source of magnesium and its compounds is seawater. Magnesium forms the second most abundant positive ion in the sea, and scientists separate Mg^{2+} from the other cations in seawater (Na^+, Ca^{2+}, and K^+, in particular) by taking advantage of the fact that magnesium hydroxide is the least soluble hydroxide of the group. Economical recovery of magnesium requires a low-cost base to treat large volumes of seawater and efficient methods for separating the $Mg(OH)_2(s)$ that precipitates from the solution. One base that is used in this way is calcined dolomite, prepared by heating dolomite to high temperatures to drive off carbon dioxide:

$$CaMg(CO_3)_2(s) \longrightarrow CaO \cdot MgO(s) + 2\ CO_2(g)$$

The greater solubility of calcium hydroxide ($K_{sp} = 5.5 \times 10^{-6}$) relative to magnesium hydroxide ($K_{sp} = 1.2 \times 10^{-11}$) leads to the reaction

$$CaO \cdot MgO(s) + Mg^{2+}(aq) + 2\ H_2O(\ell) \longrightarrow 2\ Mg(OH)_2(s) + Ca^{2+}(aq)$$

The magnesium hydroxide that is produced in this process includes not only the magnesium from the seawater but also that from the dolomite.

An interesting alternative to dolomite as a base for magnesium production is a process used off the coast of Texas (Fig. 17.17). Oyster shells (composed largely of

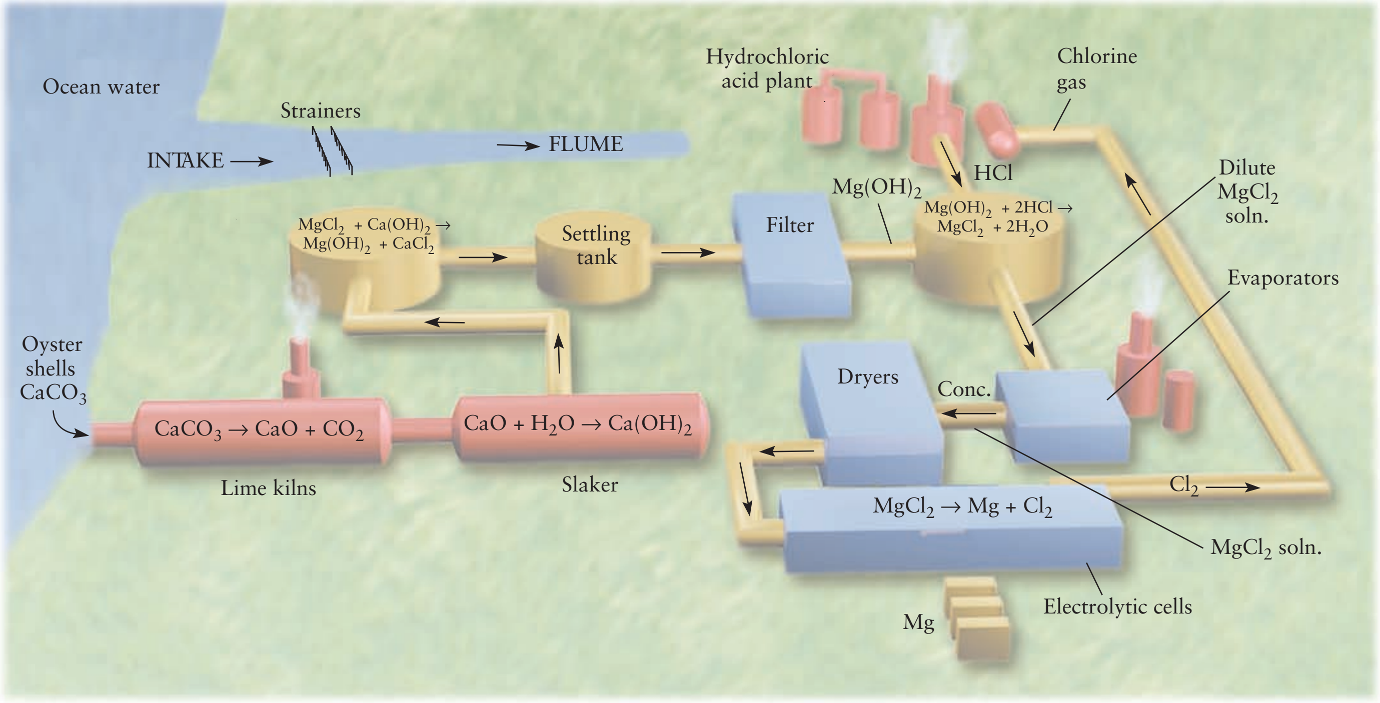


FIGURE 17.17 The production of magnesium hydroxide starts with the addition of lime (CaO) to seawater. Reaction of the magnesium hydroxide with hydrochloric acid produces magnesium chloride, which, after drying, is electrolyzed to give magnesium.

$CaCO_3$) are calcined to give lime (CaO), which is added to the seawater to yield magnesium hydroxide. The $Mg(OH)_2$ slurry (a suspension in water) is washed and filtered in huge nylon filters.

After purification, $Mg(OH)_2$ can be reacted with carbon dioxide to give magnesium carbonate, used for coating sodium chloride in table salt to prevent caking and for antacid remedies. Another alternative is to add hydrochloric acid to the magnesium hydroxide to neutralize it and yield hydrated magnesium chloride:

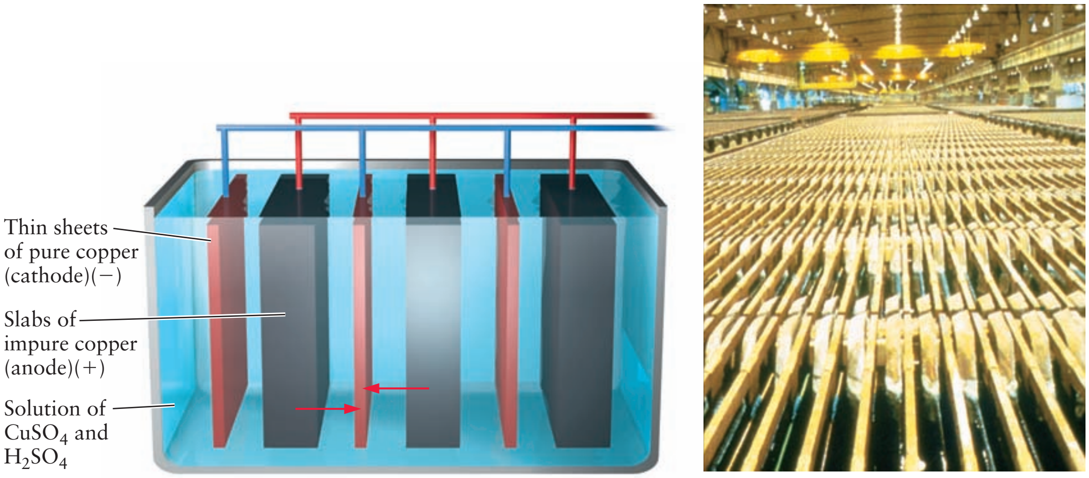
$$\mathrm{Mg(OH)_2}(s) + 2\,\mathrm{HCl}(aq) \longrightarrow \mathrm{MgCl_2}(aq) + 2\,\mathrm{H_2O}(\ell)$$

After the water is evaporated, the solid magnesium chloride is melted (m.p. 708°C) in a large steel electrolysis cell that holds as much as 10 tons of the molten salt. The steel in the cell acts as the cathode during electrolysis, with graphite anodes suspended from the top. The cell reaction is

$$\mathrm{MgCl_2}(\ell) \longrightarrow \mathrm{Mg}(\ell) + \mathrm{Cl_2}(g)$$

The molten magnesium liberated at the cathode floats to the surface and is dipped out periodically, while the chlorine released at the anodes is collected and reacted with steam at high temperatures to produce hydrochloric acid. This is recycled for further reaction with magnesium hydroxide.

Until 1918, elemental magnesium was used mainly in fireworks and flashbulbs, which took advantage of its great reactivity with the oxygen in air and the bright light given off in that reaction (see Fig. 11.6). Since then, many further uses for the metal and its alloys have been developed. Magnesium is even less dense than aluminum and is used in alloys with aluminum to lower its density and improve its resistance to corrosion under basic conditions. As discussed in Section 17.5 magnesium is used as a sacrificial anode to prevent the oxidation of another metal with which it is in contact. It is also used as a reducing agent to produce other metals such as titanium, uranium, and beryllium from their compounds.



ASARCO

FIGURE 17.18 In the electrolytic refining of copper, many slabs of impure copper, which serve as anodes, alternate with thin sheets of pure copper (the cathodes). Both are dipped into a dilute acidic solution of copper. As the copper is oxidized from the impure anodes, it enters the solution as Cu^{2+} and migrates to the cathodes, where it plates out in purer form.

Electrorefining and Electroplating

Metals that have been produced by pyrometallurgical methods, such as copper, silver, nickel, and tin, are too impure for many purposes, and **electrorefining** is used to purify them further. Crude metallic copper is cast into slabs, which are used as anodes in electrolysis cells that contain a solution of $CuSO_4$ in aqueous H_2SO_4. Thin sheets of pure copper serve as cathodes, and the copper that dissolves at the anodes is deposited in purer form on the cathodes (Fig. 17.18). Impurities that are more easily oxidized than copper, such as nickel, dissolve along with the copper but remain in solution; elements that are less easily oxidized, such as silver and gold, do not dissolve but fall away from the anode as a metallic slime. Periodically, the anode slime and the solution are removed and further processed for recovery of the elements they contain.

A related process is **electroplating,** in which electrolysis is used to plate out a thin layer of a metal on another material, often a second metal. In chrome plating, the piece of metal to be plated is placed in a hot bath of sulfuric acid and chromic acid (H_2CrO_4) and is made the cathode in an electrolytic cell. As current passes through the cell, chromium is reduced from the $+6$ oxidation state in chromic acid to elemental chromium and plates out on the cathode. A decorative chromium layer can be as thin as 2.5×10^{-5} cm (corresponding to 2 g of Cr per square meter of surface). Thicker layers ranging up to 10^{-2} cm are found in hard chromium plate, prized for its resistance to wear and used in automobile trim. Steel can be plated with cadmium to improve its resistance to corrosion in marine environments. Gold and silver are used both for decorative plating and (because they are good conductors of electricity) on electronic devices.

EXAMPLE 17.10

Suppose a layer of chromium 3.0×10^{-3} cm thick is to be plated onto an automobile bumper with a surface area of 2.0×10^{3} cm^2. If a current of 250 A is used, how long must current be passed through the cell to achieve the desired thickness? The density of chromium is 7.2 g cm^{-3}.

SOLUTION

The volume of the Cr is the product of the thickness of the layer and the surface area:

$$\text{volume} = (3.0 \times 10^{-3}\ \text{cm})(2.0 \times 10^{3}\ \text{cm}^2) = 6.0\ \text{cm}^3$$

The mass of chromium is the product of this volume and the density:

$$\text{mass Cr} = (6.0\ \text{cm}^3)(7.2\ \text{g cm}^{-3}) = 43.2\ \text{g}$$

From this, the number of moles of Cr that must be reduced is

$$\frac{43.2\ \text{g}}{52.00\ \text{g mol}^{-1}} = 0.831\ \text{mol Cr}$$

Because Cr is being reduced from oxidation state +6 in H_2CrO_4 to 0 in the elemental form, six electrons are required for each atom of Cr deposited. The number of moles of electrons is then

$$0.831\ \text{mol Cr} \times \left(\frac{6\ \text{mol}\ e^-}{1\ \text{mol Cr}}\right) = 4.98\ \text{mol}\ e^-$$

$$\text{total charge} = (4.98\ \text{mol})(96{,}485\ \text{C mol}^{-1}) = 4.81 \times 10^5\ \text{C}$$

The required electrolysis time is the total charge divided by the current (in amperes):

$$\text{time} = \frac{4.81 \times 10^5\ \text{C}}{250\ \text{C s}^{-1}} = 1.9 \times 10^3\ \text{s} = 32\ \text{min}$$

Related Problems: 61, 62

A DEEPER LOOK

17.7 Electrolysis of Water and Aqueous Solutions

In Section 17.6 we discussed applications of electrolysis in the extraction and purification of metals from their ore sources. Here we examine the electrolysis of water and aqueous solutions. Consider first the electrolysis of water between inert electrodes such as platinum, for which the half-cell reactions are

$$2\ H_3O^+(aq) + 2\ e^- \longrightarrow H_2(g) + 2\ H_2O(\ell) \qquad \text{(cathode)}$$

$$3\ H_2O(\ell) \longrightarrow \tfrac{1}{2}\ O_2(g) + 2\ H_3O^+(aq) + 2\ e^- \qquad \text{(anode)}$$

$$\overline{\qquad H_2O(\ell) \longrightarrow H_2(g) + \tfrac{1}{2}\ O_2(g) \qquad}$$

A practical problem immediately arises. The concentration of $H_3O^+(aq)$ and OH^- (aq) ions in pure water at 25°C is only 1.0×10^{-7} M, so the *rate* of electrolysis will be exceedingly small. This practical consideration is put aside for the moment because it does not alter the *thermodynamic* analysis.

The potential $\mathscr{E}°$ for the cathode reaction is by definition 0 V, but because the $H_3O^+(aq)$ concentration in pure water is not 1 M but 1.0×10^{-7} M, $\mathscr{E}$ differs from $\mathscr{E}°$ and equals

$$\mathscr{E}(\text{cathode}) = \mathscr{E}°(\text{cathode}) - \frac{0.0592\ \text{V}}{n_{\text{hc}}} \log Q_{\text{hc}}$$

$$= 0.00 - \frac{0.0592}{2} \log \frac{P_{H_2}}{[H_3O^+]^2}$$

If $H_2(g)$ is produced at atmospheric pressure, this simplifies to

$$\mathscr{E}(\text{cathode}) = 0.00 - \frac{0.0592\ \text{V}}{2} \log \frac{1}{(10^{-7})^2}$$

$$= -0.414\ \text{V}$$

The anode half-reaction written as a reduction (*i.e.,* in reverse) is

$$\tfrac{1}{2}\ O_2(g) + 2\ H_3O^+(aq) + 2\ e^- \longrightarrow 3\ H_2O(\ell)$$

A table of standard reduction potentials (see Appendix E) gives $\mathscr{E}° = 1.229$ V. In the present case, the $H_3O^+(aq)$ concentration is 1.0×10^{-7} M rather than 1 M, so

$$\mathscr{E}(\text{anode}) = \mathscr{E}° - \frac{0.0592\ \text{V}}{2} \log \frac{1}{(P_{O_2})^{1/2}[H_3O^+]^2}$$

$$= 1.229\ \text{V} - \frac{0.0592\ \text{V}}{2} \log \frac{1}{(10^{-7})^2}$$

$$= 0.815\ \text{V}$$

if $P_{O_2} = 1$ atm. The overall cell voltage is

$$\Delta\mathscr{E} = \mathscr{E}(\text{cathode}) - \mathscr{E}(\text{anode}) = -0.414 - 0.815\ \text{V} = -1.229\ \text{V}$$

A negative $\Delta\mathscr{E}$ means that the process does not occur spontaneously; it can be made to occur only by applying an external voltage sufficient to overcome the intrinsic negative voltage of the cell. In the electrolysis of water, this minimum external voltage, which is called the **decomposition potential** of water, is 1.229 V. When this potential difference has been applied, an overall cell reaction will occur, given by the sum of the reduction and oxidation half-reactions:

$$H_2O(\ell) \longrightarrow \tfrac{1}{2}\,O_2(g) + H_2(g)$$

Hydrogen will bubble off at the cathode and oxygen at the anode.

Suppose an external voltage is now used to electrolyze an electrolyte solution instead of pure water. The resultant products depend on the concentrations of the ions present and their half-cell potentials. In a 0.10 M NaCl solution, we could conceive of the following processes taking place:

Cathode:

$$Na^+(0.1\ \text{M}) + e^- \longrightarrow Na(s)$$

$$2\ H_3O^+(10^{-7}\ \text{M}) + 2\ e^- \longrightarrow H_2(g) + 2\ H_2O(\ell)$$

Anode:

$$Cl^-(0.1\ \text{M}) \longrightarrow \tfrac{1}{2}\,Cl_2(g) + e^-$$

$$3\ H_2O(\ell) \longrightarrow \tfrac{1}{2}\,O_2(g) + 2\ H_3O^+\ (10^{-7}\ \text{M}) + 2\ e^-$$

In each of these pairs of possible processes, which one will actually occur?

For the first half-reaction the reduction potential is

$$\mathscr{E}(Na^+|Na) = \mathscr{E}°(Na^+|Na) - \frac{0.0592\ \text{V}}{1}\log\frac{1}{[Na^+]}$$

$$= -2.71 - 0.06 = -2.77\ \text{V}$$

Because this result is more negative than the half-cell voltage $\mathscr{E}(H_3O^+(10^{-7}\ \text{M})|\,H_2) = -0.414$ V for pure water, the reduction of $Na^+(aq)$ is impossible, and $H_2(g)$ is the cathode product.

For the third half-reaction, the reduction potential is

$$\mathscr{E}(Cl_2|Cl^-) = \mathscr{E}°(Cl_2|Cl^-) - \frac{0.0592\ \text{V}}{1}\log\frac{[Cl^-]}{P_{Cl_2}^{1/2}}$$

$$= 1.36 + 0.06 = 1.42\ \text{V}$$

Because this is more positive than the half-cell voltage $\mathscr{E}(O_2,H_3O^+(10^{-7}\ \text{M})|\,H_2O) = 0.815$ V for pure water, Cl_2 has a *greater* tendency to be reduced than O_2; therefore, Cl^- has a *lesser* tendency to be oxidized than H_2O, and the anode product is $O_2(g)$. If we try to increase the external potential above 1.229 V, all that will happen is that water will be electrolyzed at a greater rate to produce hydrogen and oxygen. Sodium and chlorine will not appear as long as sufficient water is present.

Suppose now that 0.10 M NaI is substituted for the 0.10 M NaCl solution. Sodium ions still will not be reduced; however, $\mathscr{E}(I_2|\,I^-)$ is

$$\mathscr{E}(I_2|I^-) = \mathscr{E}°(I_2|I^-) - \frac{0.0592\ \text{V}}{1}\log\,[I^-]$$

$$= 0.535 + 0.059 = 0.594\ \text{V}$$

The half-cell potential for the reduction of iodine is *less* positive than the reduction potential of $O_2(g)$ in water at pH = 7(0.815 V), so the oxidation of 0.10 M I^- occurs in preference to the oxidation of water. The anode reaction is therefore

$$I^-(0.10\ \text{M}) \longrightarrow \tfrac{1}{2}\,I_2(s) + e^-$$

and the overall cell reaction is

$$H_3O^+(10^{-7}\ \text{M}) + I^-(0.10\ \text{M}) \longrightarrow \tfrac{1}{2}\,H_2(g) + \tfrac{1}{2}\,I_2(s) + H_2O(\ell)$$

The intrinsic cell voltage is

$$\Delta\mathscr{E} = \mathscr{E}(\text{cathode}) - \mathscr{E}(\text{anode}) = -0.414 - 0.594\ \text{V} = -1.008\ \text{V}$$

When the applied voltage exceeds 1.008 V, $H_2(g)$ and $I_2(s)$ begin to form. Of course, this causes $[I^-]$ to decrease and $\mathscr{E}(I_2|\,I^-)$ to increase. When the iodide ion concentration reaches about 2×10^{-5} M, $\mathscr{E}(I_2|\,I^-)$ will have increased to 0.815 V and the external voltage required to maintain electrolysis will have increased to 1.229 V. At this point, water will start to be electrolyzed and oxygen will be produced at the anode.

Our results for the electrolysis of *neutral* aqueous solutions are summarized as follows:

1. A species can be reduced only if its reduction potential is algebraically greater than −0.414 V.
2. A species can be oxidized only if its reduction potential is algebraically smaller than 0.815 V.

In solutions with pH different from 7, these results must be modified, as shown by the following example.

EXAMPLE 17.11

An aqueous 0.10 M solution of $NiCl_2$ is electrolyzed under 1 atm pressure. Determine the products formed at the anode and the cathode and the decomposition potential, if the pH is (**a**) 7.0; (**b**) 0.0.

SOLUTION

The reduction of Ni^{2+} at the cathode has the half-cell potential

$$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$$

$$\mathscr{E}(Ni^{2+}|Ni) = \mathscr{E}°(Ni^{2+}|Ni) - \frac{0.0592\ \text{V}}{2}\log\frac{1}{[Ni^{2+}]}$$

$$= -0.23 - 0.03 = -0.26\ \text{V}$$

and the oxidation of the Cl^- at the anode has the *reduction* potential

$$\tfrac{1}{2}\,Cl_2(g) + e^- \longrightarrow Cl^-(aq)$$

$$\mathscr{E}(Cl_2|Cl^-) = \mathscr{E}°(Cl_2|Cl^-) - \frac{0.0592\ \text{V}}{2}\log\frac{[Cl^-]}{P_{Cl_2}^{1/2}}$$

$$= 1.36\ \text{V} - (0.0592\ \text{V})\log 0.2 = 1.40\ \text{V}$$

(**a**) In neutral solution the cathode half-reaction is

$$Ni^{2+}(aq) + 2\ e^- \longrightarrow Ni(s)$$

because $\mathscr{E}(Ni^{2+}|\,Ni) = -0.26\ \text{V} > -0.414$ V. The anode half-reaction is

$$3\ H_2O(\ell) \longrightarrow 2\ H_3O^+(10^{-7}\ \text{M}) + \tfrac{1}{2}\,O_2(g) + 2\ e^-$$

because $\mathscr{E}(Cl_2|\,Cl^-) = 1.40\ \text{V} > 0.815$ V (the reduction potential for this half-reaction). The cell voltage is

$$\Delta\mathscr{E} = \mathscr{E}(\text{cathode}) - \mathscr{E}(\text{anode}) = -0.26 - 0.815\ \text{V} = -1.08\ \text{V}$$

so the decomposition potential is 1.08 V.

(b) In 1.0 M acid solution (pH = 0.0), the anode half-reaction is still

$$3\ H_2O(\ell) \longrightarrow 2\ H_3O^+(1\ \text{M}) + \tfrac{1}{2}\ O_2(g) + 2\ e^-$$

The reduction potential for this reaction is now $\mathscr{E}_{hc} = \mathscr{E}^\circ_{hc} =$ 1.229 V, which is still less than 1.40 V, the reduction potential for the competing reaction involving chlorine.

The cathode half-reaction now becomes

$$2\ H_3O^+(1\ \text{M}) + 2\ e^- \longrightarrow H_2(g) + 2\ H_2O(\ell)$$

because $\mathscr{E}(H_3O^+|H_2) = 0.0\ \text{V} > -0.26\ \text{V}$ for $\mathscr{E}(Ni^{2+}|Ni)$. We now have

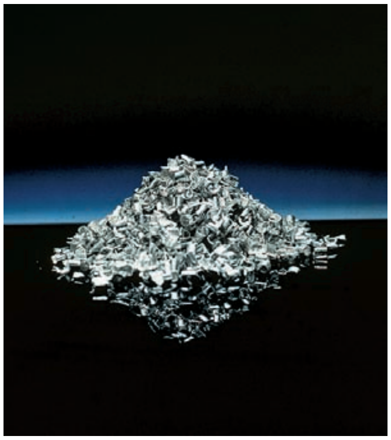
$$\Delta\mathscr{E} = \mathscr{E}(\text{cathode}) - \mathscr{E}(\text{anode}) = 0.00 - 1.229 = -1.229\ \text{V}$$

so the decomposition potential of the solution is now 1.229 V, just as it is for pure water.

Related Problems: 63, 64

CHAPTER SUMMARY

Electrochemical reactions are an important class of oxidation–reduction (redox) reactions that interconvert chemical and electrical energy. The free energy released in a spontaneous chemical reaction can be used to generate electricity, or electrical energy can be provided from an external source to drive chemical reactions that are not normally spontaneous. The key to this flexibility is the separation of the oxidation and reduction parts of the reaction with the electrons being transferred through an external circuit. Electrochemistry is enormously important in many existing technologies such as energy conversion and storage, and large-scale chemical syntheses of commodity chemicals like chlorine. It is also an enabling science for alternative energy sources, such as fuel cells for large scale deployment in transportation and small dedicated power plants, and for the efficient capture and storage of solar energy in batteries and as chemical energy in hydrogen produced by photoelectrochemical water splitting. The cell potential $\Delta\mathscr{E}$ is simply related to the Gibbs free energy for an electrochemical reaction, providing a quantitative measure of the driving force for the reaction. The cell potential goes to zero for reactions at equilibrium, so the standard cell potential $\Delta\mathscr{E}^\circ$ is a direct measure of the equilibrium constant in electrochemical reactions. Because $\mathscr{E}$ is a state function, the equilibrium constant for a particular reaction is the same whether carried out electrochemically or otherwise, so electrochemistry is a powerful way to measure equilibrium constants for reactions that can be difficult to measure in other environments.



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A pile of manganese metal.

CUMULATIVE EXERCISE

Manganese

Manganese is the 12th most abundant element on the earth's surface. Its most important ore source is pyrolusite (MnO_2). The preparation and uses of manganese and its compounds (which range up to +7 in oxidation state) are intimately bound up with electrochemistry.

(a) Elemental manganese in a state of high purity can be prepared by electrolyzing aqueous solutions of Mn^{2+}. At which electrode (anode or cathode) does the Mn appear? Electrolysis is also used to make MnO_2 in high purity from Mn^{2+} solutions. At which electrode does the MnO_2 appear?

(b) The Winkler method is an analytical procedure for determining the amount of oxygen dissolved in water. In the first step, $Mn(OH)_2(s)$ is oxidized by gaseous oxygen to $Mn(OH)_3(s)$ in basic aqueous solution. Write the oxidation and reduction half-equations for this step, and write the balanced overall equation. Then use Appendix E to calculate the standard voltage that would be measured if this reaction were carried out in an electrochemical cell.

(c) Calculate the equilibrium constant at 25°C for the reaction in part (b).

(d) In the second step of the Winkler method, the $Mn(OH)_3$ is acidified to give Mn^{3+} and iodide ion is added. Will Mn^{3+} spontaneously oxidize I^-? Write a balanced equation for its reaction with I^-, and use data from Appendix E to calculate its equilibrium constant. Titration of the I_2 produced completes the use of the Winkler method.

(e) Manganese(IV) is an even stronger oxidizing agent than manganese(III). It oxidizes zinc to Zn^{2+} in the dry cell. Such a battery has a cell voltage of 1.5 V. Calculate the electrical work done by this battery in 1.00 hour if it produces a steady current of 0.70 A.

(f) Calculate the mass of zinc reacting in the process described in part (e).

(g) The reduction potential of permanganate ion (+7 oxidation state) in acidic aqueous solution is given by

$$MnO_4^-(aq) + 8\ H_3O^+(aq) + 5\ e^- \longrightarrow Mn^{2+}(aq) + 12\ H_2O(\ell) \quad \mathscr{E}^\circ = 1.491\text{V}$$

whereas that of the analogous fifth-period species, pertechnetate ion, is

$$TcO_4^-(aq) + 8\ H_3O^+(aq) + 5\ e^- \longrightarrow Tc^{2+}(aq) + 12\ H_2O(\ell) \quad \mathscr{E}^\circ = 0.500\text{V}$$

Which is the stronger oxidizing agent, permanganate ion or pertechnetate ion?

(h) A galvanic cell is made from two half-cells. In the first, a platinum electrode is immersed in a solution at pH 2.00 that is 0.100 M in both MnO_4^- and Mn^{2+}. In the second, a zinc electrode is immersed in a 0.0100 M solution of $Zn(NO_3)_2$. Calculate the cell voltage that will be measured.

Answers

(a) Mn appears at the cathode and MnO_2 at the anode.

(b)

$$\begin{array}{rll} Mn(OH)_2(s) + OH^-(aq) \longrightarrow Mn(OH)_3(s) + e^- & & \text{(oxidation)} \\ O_2(g) + 2\ H_2O(\ell) + 4\ e^- \longrightarrow 4\ OH^-(aq) & & \text{(reduction)} \\ \hline 4\ Mn(OH)_2(s) + O_2(g) + 2\ H_2O(\ell) \longrightarrow 4\ Mn(OH)_3(s) & & \\ & \Delta\mathscr{E}^\circ = 0.401 - (-0.40) = 0.80\ \text{V} & \end{array}$$

(c) $K = 1 \times 10^{54}$

(d) Mn^{3+} will spontaneously oxidize I^-.

$$2\ Mn^{3+}(aq) + 2\ I^-(aq) \longrightarrow 2\ Mn^{2+}(aq) + I_2(s) \qquad K = 9 \times 10^{32}$$

(e) 3.8×10^3 J

(f) 0.85 g Zn is oxidized.

(g) Permanganate ion

(h) 2.12 V

CHAPTER REVIEW

- Electrochemical reactions are oxidation–reduction reactions that interconvert chemical and electrical energy.
- The free energy released in spontaneous chemical reactions conducted in a galvanic cell is converted to electrical energy, which is transferred through an external circuit to be stored or converted into work.

- Electrical energy provided through an external circuit to an electrolytic cell drives reactions that are not spontaneous, converting electrical energy into chemical potential energy.
- Electrodes in electrochemical cells are immersed in electrolytes in separate containers. Wires connect the electrodes to form an external circuit that includes meters to measure the cell potential (voltage) and current. A salt bridge transports ions between the two containers to maintain electrical neutrality.
- The electrode at which oxidation occurs is called the anode and the electrode at which reduction occurs is called the cathode.
- The number of moles of a substance that is oxidized or reduced in an electrochemical reaction is proportional to the number of moles of electrons passed through the cell. One mole of electrons is 96,485 C, and it is called the Faraday constant, $\mathcal{F}$.
- $\Delta\mathcal{E}$, the electrical potential difference or the cell potential, is the change in potential energy per unit of charge as electrons move between regions with different potentials.

  $\Delta\mathcal{E}$ is the driving force for electrochemical reactions.

  Because the charge of the electron is negative, spontaneous processes are those for which $\Delta\mathcal{E}$ increases.

  $\Delta\mathcal{E}$ is measured in joules per coulomb ($\mathrm{J\ C^{-1}}$) or volts (V) in SI units.
- The electrical work done by a galvanic cell on the surroundings is $w_{\text{elec}} = -Q\Delta\mathcal{E}$.
- The reversible work done per mol of electrons is the change in the Gibbs free energy, $\Delta G = w_{\text{elec}} - n\mathcal{F}\,\Delta\mathcal{E}$. The standard cell potential is related to the standard free energy change by $\Delta G° = w_{\text{elec}} = n\mathcal{F}\,\Delta\mathcal{E}°$.
- Half-cell reactions provide a convenient way to balance electrochemical reactions and to calculate cell potentials.

  Half-cell reactions have the form $\mathrm{X^{n+}}(aq) + \mathrm{n}e^- \longrightarrow \mathrm{X}(aq)$ for the reduction reaction and $\mathrm{Y}(aq) \longrightarrow \mathrm{Y^{n+}}(aq) + \mathrm{n}e^-$ for the oxidation reaction.

  The overall reaction is written as the sum of a reduction half-cell reaction and an oxidation half-cell reaction.

  A set of standard reduction potentials has been established by measuring the cell potentials of a number of half-cell reactions against the half-cell reduction of $\mathrm{H_3O^+}$ to form hydrogen gas and water. This reaction has been arbitrarily assigned a standard reduction potential $\mathcal{E}° = 0$.

  $\Delta\mathcal{E}° = \mathcal{E}°(\text{cathode}) - \mathcal{E}°(\text{anode})$.
- Cell potentials can be calculated for conditions other than standard state conditions using the Nernst equation.

  $\Delta\mathcal{E} = \Delta\mathcal{E}° = \dfrac{RT}{n\mathcal{F}} \ln Q$ where Q is the reaction quotient discussed in Section 14.6.

  At 25°C the Nernst equation can be written as $\Delta\mathcal{E} = \Delta\mathcal{E}° - \dfrac{0.0592\ \text{V}}{n} \log_{10} Q$ which is more convenient for quick calculations and estimates.
- Measuring equilibrium constants is one of the most important applications of electrochemistry. Since $\Delta\mathcal{E}° = 0$ at equilibrium (no thermodynamic driving force for change) and $Q = K$, the Nernst equation can be rearranged to give $\Delta\mathcal{E}° = \dfrac{0.0592\ \text{V}}{n} \log_{10} K$ allowing equilibrium constants to be determined simply by measuring standard cell potentials.

CONCEPTS & SKILLS

After studying this chapter and working the problems that follow, you should be able to:

1. Define the terms *anode* and *cathode* and give the convention that is used to represent a galvanic cell (Section 17.1, problems 1–2).
2. Use Faraday's laws to calculate the quantities of substances produced or consumed at the electrodes of electrochemical cells in relation to the total charge passing through the circuit (Section 17.1, problems 3–10).
3. Explain the relationship between the free energy change in a galvanic cell and the amount of electrical work (Section 17.2, problems 11–12).
4. Combine half-cell reactions and their standard reduction potentials to obtain the overall reactions and standard voltages of electrochemical cells (Section 17.2, problems 13–16).
5. Combine half-reactions and their standard reduction potentials to form other half-reactions and their standard reduction potentials (Section 17.2, problems 23–24).
6. Use reduction potential diagrams to determine strengths of oxidizing and reducing agents and stability toward disproportionation (Section 17.2, problems 25–26).
7. Apply the Nernst equation to calculate the voltage of a cell in which reactants and products are not in their standard states and to calculate the value of an equilibrium constant from the voltage of an electrochemical cell (Section 17.3, problems 27–38).
8. Describe the principles that underlie the use of electrochemical cells as pH meters (Section 17.3, problems 39–40).
9. Discuss the electrochemistry of a primary battery and contrast it with that of a secondary battery and a fuel cell (Section 17.4, problems 43–50).
10. Discuss the electrochemical corrosion of metals and describe measures that may be used to minimize it (Section 17.5, problems 51–54).
11. Describe the Hall–Héroult process for the production of aluminum and the methods used to recover magnesium from seawater (Section 17.6, problems 57–58).
12. Use Faraday's laws to relate current to metal deposited in electrorefining and electroplating operations (Section 17.6, problems 61–62).
13. Predict the products liberated at the anode and cathode of an electrolysis cell with a given aqueous electrolyte composition (Section 17.7, problems 63–64).

KEY EQUATIONS

$$I = \frac{Q}{t}$$ **(Section 17.1)**

$$w_{\text{elec}} = -Q\Delta\mathscr{E}$$ **(Section 17.2)**

$$-w_{\text{elec,max}} = |\Delta G| \qquad \text{(at constant } T \text{ and } P\text{)}$$ **(Section 17.2)**

$$\Delta G° = -n\mathscr{F}\,\Delta\mathscr{E}°$$ **(Section 17.2)**

$$\Delta\mathscr{E}° = \mathscr{E}°(\text{cathode}) - \mathscr{E}°(\text{anode})$$ **(Section 17.2)**

$$\Delta\mathscr{E} = \Delta\mathscr{E}^\circ - \frac{RT}{n\mathscr{F}} \ln Q \qquad \text{(Section 17.3)}$$

$$\Delta\mathscr{E} = \Delta\mathscr{E}^\circ - \frac{0.0592\ \text{V}}{n} \log_{10} Q \quad \text{(at 25°C)} \qquad \text{(Section 17.3)}$$

$$\log_{10} K = \frac{n}{0.0592\ \text{V}} \Delta\mathscr{E}^\circ \quad \text{(at 25°C)} \qquad \text{(Section 17.3)}$$

PROBLEMS

Answers to problems whose numbers are boldface appear in Appendix G. Problems that are more challenging are indicated with asterisks.

Electrochemical Cells

1. Diagram the following galvanic cell, indicating the direction of flow of electrons in the external circuit and the motion of ions in the salt bridge.

$$\text{Pt}(s)|\text{Cr}^{2+}(aq), \text{Cr}^{3+}(aq)||\text{Cu}^{2+}(aq)|\text{Cu}(s)$$

Write a balanced equation for the overall reaction in this cell.

2. Diagram the following galvanic cell, indicating the direction of flow of electrons in the external circuit and the motion of ions in the salt bridge.

$$\text{Ni}(s)|\text{Ni}^{2+}(aq)||\text{HCl}(aq)|\text{H}_2(g)|\text{Pt}(s)$$

Write a balanced equation for the overall reaction in this cell.

3. A quantity of electricity equal to 6.95×10^4 C passes through an electrolytic cell that contains a solution of $Sn^{4+}(aq)$ ions. Compute the maximum chemical amount, in moles, of Sn(*s*) that can be deposited at the cathode.

4. A quantity of electricity equal to 9.263×10^4 C passes through a galvanic cell that has an Ni(*s*) anode. Compute the maximum chemical amount, in moles, of $Ni^{2+}(aq)$ that can be released into solution.

5. A galvanic cell is constructed that has a zinc anode immersed in a $Zn(NO_3)_2$ solution and a platinum cathode immersed in an NaCl solution equilibrated with $Cl_2(g)$ at 1 atm and 25°C. A salt bridge connects the two half-cells.
(a) Write a balanced equation for the cell reaction.
(b) A steady current of 0.800 A is observed to flow for a period of 25.0 minutes. How much charge passes through the circuit during this time? How many moles of electrons is this charge equivalent to?
(c) Calculate the change in mass of the zinc electrode.
(d) Calculate the volume of gaseous chlorine generated or consumed as a result of the reaction.

6. A galvanic cell consists of a cadmium cathode immersed in a $CdSO_4$ solution and a zinc anode immersed in a $ZnSO_4$ solution. A salt bridge connects the two half-cells.
(a) Write a balanced equation for the cell reaction.
(b) A current of 1.45 A is observed to flow for a period of 2.60 hours. How much charge passes through the circuit during this time? How many moles of electrons is this charge equivalent to?
(c) Calculate the change in mass of the zinc electrode.
(d) Calculate the change in mass of the cadmium electrode.

7. An acidic solution containing copper ions is electrolyzed, producing gaseous oxygen (from water) at the anode and copper at the cathode. For every 16.0 g of oxygen generated, 63.5 g of copper plates out. What is the oxidation state of the copper in the solution?

8. Michael Faraday reported that passing electricity through one solution liberated 1 mass of hydrogen at the cathode and 8 masses of oxygen at the anode. The same quantity of electricity liberated 36 masses of chlorine at the anode and 58 masses of tin at the cathode from a second solution. What were the oxidation states of hydrogen, oxygen, chlorine, and tin in these solutions?

9. Liquid potassium chloride, KCl(ℓ), is decomposed in an electrolytic cell to form potassium and chlorine. Liquid KCl consists of K^+ and Cl^- ions.
(a) Write balanced equations for the half-cell reactions at the anode and at the cathode and for the overall cell reaction.
(b) If a current of 2.00 A is passed through the cell for a period of 5.00 hours, calculate the mass of metal deposited and of gas liberated.

10. In the Hall–Héroult process for the electrolytic production of aluminum, Al^{3+} ions from Al_2O_3 dissolved in molten cryolite (Na_3AlF_6) are reduced to Al(ℓ) while carbon (graphite) is oxidized to CO_2 by reaction with oxide ions.
(a) Write balanced equations for the half-reactions at the anode and at the cathode and for the overall cell reaction.
(b) If a current of 50,000 A is passed through the cell for a period of 24 hours, what mass of aluminum will be recovered?

The Gibbs Free Energy and Cell Voltage

11. A $Ni|Ni^{2+}||Ag^+|Ag$ galvanic cell is constructed in which the standard cell voltage is 1.03 V. Calculate the free energy change at 25°C when 1.00 g of silver plates out, if all concentrations remain at their standard value of 1 M throughout the process. What is the maximum electrical work done by the cell on its surroundings during this experiment?

12. A $Zn|Zn^{2+}||Co^{2+}|Co$ galvanic cell is constructed in which the standard cell voltage is 0.48 V. Calculate the free energy change at 25°C per gram of zinc lost at the anode, if all concentrations remain at their standard value of 1 M throughout the process. What is the maximum electrical work done by the cell on its surroundings during this experiment?

13. A galvanic cell is constructed in which a $Br_2|Br^+$ half-cell is connected to a $Co^{2+}|Co$ half-cell.

(a) By referring to Appendix E, write balanced chemical equations for the half-reactions at the anode and the cathode and for the overall cell reaction.

(b) Calculate the cell voltage, assuming that all reactants and products are in their standard states.

14. A galvanic cell is constructed in which a $Pt|Fe^{2+}, Fe^{3+}$ half-cell is connected to a $Cd^{2+}|Cd$ half-cell.

(a) By referring to Appendix E, write balanced chemical equations for the half-reactions at the anode and the cathode and for the overall cell reaction.

(b) Calculate the cell voltage, assuming that all reactants and products are in their standard states.

15. In a galvanic cell, one half-cell consists of a zinc strip dipped into a 1.00 M solution of $Zn(NO_3)_2$. In the second half-cell, solid indium adsorbed on graphite is in contact with a 1.00 M solution of $In(NO_3)_3$. Indium is observed to plate out as the galvanic cell operates, and the initial cell voltage is measured to be 0.425 V at 25°C.

(a) Write balanced equations for the half-reactions at the anode and the cathode.

(b) Calculate the standard reduction potential of an $In^{3+}|In$ half-cell. Consult Appendix E for the reduction potential of the $Zn^{2+}|Zn$ electrode.

16. In a galvanic cell, one half-cell consists of gaseous chlorine bubbled over a platinum electrode at a pressure of 1.00 atm into a 1.00 M solution of NaCl. The second half-cell has a strip of solid gallium immersed in a 1.00 M $Ga(NO_3)_3$ solution. The initial cell voltage is measured to be 1.918 V at 25°C, and as the cell operates, the concentration of chloride ion is observed to increase.

(a) Write balanced equations for the half-reactions at the anode and the cathode.

(b) Calculate the standard reduction potential of a $Ga^{3+}|Ga$ half-cell. Consult Appendix E for the reduction potential of the $Cl_2|Cl^-$ electrode.

17. Would you expect powdered solid aluminum to act as an oxidizing agent or as a reducing agent?

18. Would you expect potassium perchlorate, $KClO_4(aq)$, in a concentrated acidic solution to act as an oxidizing agent or as a reducing agent?

19. Bromine is sometimes used in place of chlorine as a disinfectant in swimming pools. If the effectiveness of a chemical as a disinfectant depends solely on its strength as an oxidizing agent, do you expect bromine to be better or worse than chlorine as a disinfectant, at a given concentration?

20. Many bleaches, including chlorine and its oxides, oxidize dye compounds in cloth. Predict which of the following will be the strongest bleach at a given concentration and pH 0: $NaClO_3(aq)$, $NaClO(aq)$, $Cl_2(aq)$. How does the strongest chlorine-containing bleach compare in strength with ozone, $O_3(g)$?

21. Suppose you have the following reagents available at pH 0, atmospheric pressure, and 1 M concentration:

$$Co(s),\ Ag^+(aq),\ Cl^-(aq),\ Cr(s),\ BrO_3^-(aq),\ I_2(s)$$

(a) Which is the strongest oxidizing agent?

(b) Which is the strongest reducing agent?

(c) Which reagent will reduce $Pb^{2+}(aq)$ while leaving $Cd^{2+}(aq)$ unreacted?

22. Suppose you have the following reagents available at pH 0, atmospheric pressure, and 1 M concentration:

$$Sc(s),\ Hg_2^{2+}(aq),\ Cr_2O_7^{2-}(aq),\ H_2O_2(aq),\ Sn^{2+}(aq),\ Ni(s)$$

(a) Which is the strongest oxidizing agent?

(b) Which is the strongest reducing agent?

(c) Which reagent will oxidize Fe(s) while leaving Cu(s) unreacted?

23. (a) Use the data from Appendix E to calculate the half-cell potential $\mathscr{E}°$ for the half-reaction

$$Mn^{3+}(aq) + 3\,e^- \longrightarrow Mn(s)$$

(b) Consider the disproportionation reaction

$$3\,Mn^{2+}(aq) \rightleftharpoons Mn(s) + 2\,Mn^{3+}(aq)$$

Will Mn^{2+} disproportionate in aqueous solution?

24. The following standard reduction potentials have been measured in aqueous solution at 25°C:

$$Tl^{3+} + e^- \longrightarrow Tl^{2+} \qquad \mathscr{E}° = -0.37\text{ V}$$

$$Tl^{3+} + 2\,e^- \longrightarrow Tl^{+} \qquad \mathscr{E}° = 1.25\text{ V}$$

(a) Calculate the half-cell potential for the half-reaction

$$Tl^{2+} + e^- \longrightarrow Tl^+$$

(b) Consider the disproportionation reaction

$$2\,Tl^{2+}(aq) \rightleftharpoons Tl^{3+}(aq) + Tl^+(aq)$$

Will Tl^{2+} disproportionate in aqueous solution?

25. The following reduction potentials are measured at pH 0:

$$BrO_3^- + 6\,H_3O^+ + 5\,e^- \longrightarrow \tfrac{1}{2}\,Br_2(\ell) + 9\,H_2O \qquad \mathscr{E}° = 1.52\text{ V}$$

$$Br_2(\ell) + 2\,e^- \longrightarrow 2\,Br^- \qquad \mathscr{E}° = 1.065\text{ V}$$

(a) Will bromine disproportionate spontaneously in acidic solution?

(b) Which is the stronger reducing agent at pH 0: $Br_2(\ell)$ or Br^-?

26. The following reduction potentials are measured at pH 14:

$$ClO^- + H_2O + 2\,e^- \longrightarrow Cl^- + 2\,OH^- \qquad \mathscr{E}° = 0.90\text{ V}$$

$$ClO_2^- + H_2O + 2\,e^- \longrightarrow ClO^- + 2\,OH^- \qquad \mathscr{E}° = 0.59\text{ V}$$

(a) Will ClO^- disproportionate spontaneously in basic solution?

(b) Which is the stronger reducing agent at pH 14: ClO^- or Cl^-?

Concentration Effects and the Nernst Equation

27. A galvanic cell is constructed that carries out the reaction

$$Pb^{2+}(aq) + 2\,Cr^{2+}(aq) \longrightarrow Pb(s) + 2\,Cr^{3+}(aq)$$

If the initial concentration of $Pb^{2+}(aq)$ is 0.15 M, that of $Cr^{2+}(aq)$ is 0.20 M, and that of $Cr^{3+}(aq)$ is 0.0030 M, calculate the initial voltage generated by the cell at 25°C.

28. A galvanic cell is constructed that carries out the reaction

$$2\ \mathrm{Ag}(s) + \mathrm{Cl_2}(g) \longrightarrow 2\ \mathrm{Ag^+}(aq) + 2\ \mathrm{Cl^-}(aq)$$

If the partial pressure of $Cl_2(g)$ is 1.00 atm, the initial concentration of $Ag^+(aq)$ is 0.25 M, and that of $Cl^-(aq)$ is 0.016 M, calculate the initial voltage generated by the cell at 25°C.

29. Calculate the reduction potential for a $\mathrm{Pt}|\mathrm{Cr^{3+}}, \mathrm{Cr^{2+}}$ half-cell in which $[Cr^{3+}]$ is 0.15 M and $[Cr^{2+}]$ is 0.0019 M.

30. Calculate the reduction potential for an $\mathrm{I_2}(s)|\mathrm{I^-}$ half-cell in which $[I^-]$ is 1.5×10^{-6} M.

31. An $\mathrm{I_2}(s)|\mathrm{I^-}(1.00\ \mathrm{M})$ half-cell is connected to an $\mathrm{H_3O^+}|\mathrm{H_2}$ (1 atm) half-cell in which the concentration of the hydronium ion is unknown. The measured cell voltage is 0.841 V, and the $\mathrm{I_2}|\mathrm{I^-}$ half-cell is the cathode. What is the pH in the $\mathrm{H_3O^+}|\mathrm{H_2}$ half-cell?

32. A $\mathrm{Cu^{2+}}(1.00\ \mathrm{M})|\mathrm{Cu}$ half-cell is connected to a $\mathrm{Br_2}(\ell)|\mathrm{Br^-}$ half-cell in which the concentration of bromide ion is unknown. The measured cell voltage is 0.963 V, and the $\mathrm{Cu^{2+}}|\mathrm{Cu}$ half-cell is the anode. What is the bromide ion concentration in the $\mathrm{Br_2}(\ell)|\mathrm{Br^-}$ half-cell?

33. The following reaction occurs in an electrochemical cell:

$$3\ \mathrm{HClO_2}(aq) + 2\ \mathrm{Cr^{3+}}(aq) + 12\ \mathrm{H_2O}(\ell) \longrightarrow$$
$$3\ \mathrm{HClO}(aq) + \mathrm{Cr_2O_7^{2-}}(aq) + 8\ \mathrm{H_3O^+}(aq)$$

(a) Calculate $\Delta\mathcal{E}^\circ$ for this cell.
(b) At pH 0, with $[\mathrm{Cr_2O_7^{2-}}] = 0.80$ M, $[\mathrm{HClO_2}] = 0.15$ M, and $[\mathrm{HClO}] = 0.20$ M, the cell voltage is found to be 0.15 V. Calculate the concentration of $Cr^{3+}(aq)$ in the cell.

34. A galvanic cell is constructed in which the overall reaction is

$$\mathrm{Cr_2O_7^{2-}}(aq) + 14\ \mathrm{H_3O^+}(aq) + 6\ \mathrm{I^-}(aq) \longrightarrow$$
$$2\ \mathrm{Cr^{3+}}(aq) + 3\ \mathrm{I_2}(s) + 21\ \mathrm{H_2O}(\ell)$$

(a) Calculate $\Delta\mathcal{E}^\circ$ for this cell.
(b) At pH 0, with $[\mathrm{Cr_2O_7^{2-}}] = 1.5$ M and $[\mathrm{I^-}] = 0.40$ M, the cell voltage is found to equal 0.87 V. Calculate the concentration of $Cr^{3+}(aq)$ in the cell.

35. By using the half-cell potentials in Appendix E, calculate the equilibrium constant at 25°C for the reaction in problem 33. Dichromate ion ($\mathrm{Cr_2O_7^{2-}}$) is orange, and Cr^{3+} is light green in aqueous solution. If 2.00 L of 1.00 M $HClO_2$ solution is added to 2.00 L of 0.50 M $Cr(NO_3)_3$ solution, what color will the resulting solution have?

36. By using the half-cell potentials in Appendix E, calculate the equilibrium constant at 25°C for the reaction

$$6\ \mathrm{Hg^{2+}}(aq) + 2\ \mathrm{Au}(s) \rightleftarrows 3\ \mathrm{Hg_2^{2+}}(aq) + 2\ \mathrm{Au^{3+}}(aq)$$

If 1.00 L of a 1.00 M $Au(NO_3)_3$ solution is added to 1.00 L of a 1.00 M $Hg_2(NO_3)_2$ solution, calculate the concentrations of Hg^{2+}, Hg_2^{2+}, and Au^{3+} at equilibrium.

37. The following standard reduction potentials have been determined for the aqueous chemistry of indium:

$$\mathrm{In^{3+}}(aq) + 2\ e^- \longrightarrow \mathrm{In^+}(aq) \qquad \mathcal{E}^\circ = -0.40\ \mathrm{V}$$
$$\mathrm{In^+}(aq) + e^- \longrightarrow \mathrm{In}(s) \qquad \mathcal{E}^\circ = -0.21\ \mathrm{V}$$

Calculate the equilibrium constant (K) for the disproportionation of $In^+(aq)$ at 25°C.

$$3\ \mathrm{In^+}(aq) \rightleftarrows 2\ \mathrm{In}(s) + \mathrm{In^{3+}}(aq)$$

38. Use data from Appendix E to compute the equilibrium constant for the reaction

$$\mathrm{Hg^{2+}}(aq) + \mathrm{Hg}(\ell) \rightleftarrows \mathrm{Hg_2^{2+}}(aq)$$

39. A galvanic cell consists of a $\mathrm{Pt}|\mathrm{H_3O^+}(1.00\ \mathrm{M})|\mathrm{H_2}(g)$ cathode connected to a $\mathrm{Pt}|\mathrm{H_3O^+}(aq)|\mathrm{H_2}(g)$ anode in which the concentration of H_3O^+ is unknown but is kept constant by the action of a buffer consisting of a weak acid, HA(0.10 M), mixed with its conjugate base, A^-(0.10 M). The measured cell voltage is $\Delta\mathcal{E} = 0.150$ V at 25°C, with a hydrogen pressure of 1.00 atm at both electrodes. Calculate the pH in the buffer solution, and from it determine the K_a of the weak acid.

40. In a galvanic cell, the cathode consists of a $\mathrm{Ag^+}(1.00\ \mathrm{M})|\mathrm{Ag}$ half-cell. The anode is a platinum wire, with hydrogen bubbling over it at 1.00-atm pressure, that is immersed in a buffer solution containing benzoic acid and sodium benzoate. The concentration of benzoic acid (C_6H_5COOH) is 0.10 M, and that of benzoate ion ($C_6H_5COO^-$) is 0.050 M. The overall cell reaction is then

$$\mathrm{Ag^+}(aq) + \tfrac{1}{2}\ \mathrm{H_2}(g) + \mathrm{H_2O}(\ell) \longrightarrow \mathrm{Ag}(s) + \mathrm{H_3O^+}(aq)$$

and the measured cell voltage is 1.030 V. Calculate the pH in the buffer solution and determine the K_a of benzoic acid.

41. A galvanic cell is constructed in which the overall reaction is

$$\mathrm{Br_2}(\ell) + \mathrm{H_2}(g) + 2\ \mathrm{H_2O}(\ell) \longrightarrow 2\ \mathrm{Br^-}(aq) + 2\ \mathrm{H_3O^+}(aq)$$

(a) Calculate $\Delta\mathcal{E}^\circ$ for this cell.
(b) Silver ions are added until AgBr precipitates at the cathode and $[Ag^+]$ reaches 0.060 M. The cell voltage is then measured to be 1.710 V at pH = 0 and $P_{\mathrm{H_2}} = 1.0$ atm. Calculate $[Br^-]$ under these conditions.
(c) Calculate the solubility product constant K_{sp} for AgBr.

42. A galvanic cell is constructed in which the overall reaction is

$$\mathrm{Pb}(s) + 2\ \mathrm{H_3O^+}(aq) \longrightarrow \mathrm{Pb^{2+}}(aq) + \mathrm{H_2}(g) + 2\ \mathrm{H_2O}(\ell)$$

(a) Calculate $\Delta\mathcal{E}^\circ$ for this cell.
(b) Chloride ions are added until $PbCl_2$ precipitates at the anode and $[Cl^-]$ reaches 0.15 M. The cell voltage is then measured to be 0.22 V at pH = 0 and $P_{\mathrm{H_2}} = 1.0$ atm. Calculate $[Pb^{2+}]$ under these conditions.
(c) Calculate the solubility product constant K_{sp} of $PbCl_2$.

Batteries and Fuel Cells

43. Calculate the voltage $\Delta\mathcal{E}^\circ$ of a lead–acid cell if all reactants and products are in their standard states. What will be the voltage if six such cells are connected in series?

44. Calculate the standard voltage of the zinc–mercuric oxide cell shown in Figure 17.7. (*Hint:* The easiest way to proceed is to calculate ΔG° for the corresponding overall reaction, and then find $\Delta\mathcal{E}^\circ$ from it.) Take $\Delta_f^\circ(\mathrm{Zn(OH)_2}(s)) = -553.5$ kJ mol^{-1}.

45. **(a)** What quantity of charge (in coulombs) is a fully charged 12-V lead–acid storage battery theoretically capable of furnishing if the spongy lead available for reaction at the anodes weighs 10 kg and there is excess PbO_2?

(b) What is the theoretical maximum amount of work (in joules) that can be obtained from this battery?

46. **(a)** What quantity of charge (in coulombs) is a fully charged 1.34-V zinc–mercuric oxide watch battery theoretically capable of furnishing if the mass of HgO in the battery is 0.50 g?

(b) What is the theoretical maximum amount of work (in joules) that can be obtained from this battery?

47. The concentration of the electrolyte, sulfuric acid, in a lead–acid storage battery diminishes as the battery is discharged. Is a discharged battery recharged by replacing the dilute H_2SO_4 with fresh, concentrated H_2SO_4? Explain.

48. One cold winter morning the temperature is well below 0°F. In trying to start your car, you run the battery down completely. Several hours later, you return to replace your fouled spark plugs and find that the liquid in the battery has now frozen even though the air temperature is actually a bit higher than it was in the morning. Explain how this can happen.

49. Consider the fuel cell that accomplishes the overall reaction

$$H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow H_2O(\ell)$$

If the fuel cell operates with 60% efficiency, calculate the amount of electrical work generated per gram of water produced. The gas pressures are constant at 1 atm, and the temperature is 25°C.

50. Consider the fuel cell that accomplishes the overall reaction

$$CO(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow CO_2(g)$$

Calculate the maximum electrical work that could be obtained from the conversion of 1.00 mol of $CO(g)$ to $CO_2(g)$ in such a fuel cell operated with 100% efficiency at 25°C and with the pressure of each gas equal to 1 atm.

Corrosion and Its Prevention

51. Two half-reactions proposed for the corrosion of iron in the absence of oxygen are

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2\,e^-$$

$$2\,H_2O(\ell) + 2\,e^- \longrightarrow 2\,OH^-(aq) + H_2(g)$$

Calculate the standard voltage generated by a galvanic cell running this pair of half-reactions. Is the overall reaction spontaneous under standard conditions? As the pH falls from 14, will the reaction become spontaneous?

52. In the presence of oxygen, the cathode half-reaction written in the preceding problem is replaced by

$$\tfrac{1}{2}\,O_2(g) + 2\,H_3O^+(aq) + 2\,e^- \longrightarrow 3\,H_2O(\ell)$$

but the anode half-reaction is unchanged. Calculate the standard cell voltage for *this* pair of reactions operating as a galvanic cell. Is the overall reaction spontaneous under standard conditions? As the water becomes more acidic, does the driving force for the rusting of iron increase or decrease?

53. Could sodium be used as a sacrificial anode to protect the iron hull of a ship?

54. If it is shown that titanium can be used as a sacrificial anode to protect iron, what conclusion can be drawn about the standard reduction potential of its half-reaction?

$$Ti^{3+}(aq) + 3\,e^- \longrightarrow Ti(s)$$

Electrometallurgy

55. In the Downs process, molten sodium chloride is electrolyzed to produce sodium. A valuable byproduct is chlorine. Write equations representing the processes taking place at the anode and at the cathode in the Downs process.

56. The first element to be prepared by electrolysis was potassium. In 1807, Humphry Davy, then 29 years old, passed an electric current through molten potassium hydroxide (KOH), obtaining liquid potassium at one electrode and water and oxygen at the other. Write equations to represent the processes taking place at the anode and at the cathode.

57. A current of 55,000 A is passed through a series of 100 Hall–Héroult cells for 24 hours. Calculate the maximum theoretical mass of aluminum that can be recovered.

58. A current of 75,000 A is passed through an electrolysis cell containing molten $MgCl_2$ for 7.0 days. Calculate the maximum theoretical mass of magnesium that can be recovered.

59. An important use for magnesium is to make titanium. In the Kroll process, magnesium reduces titanium(IV) chloride to elemental titanium in a sealed vessel at 800°C. Write a balanced chemical equation for this reaction. What mass of magnesium is needed, in theory, to produce 100 kg of titanium from titanium(IV) chloride?

60. Calcium is used to reduce vanadium(V) oxide to elemental vanadium in a sealed steel vessel. Vanadium is used in vanadium steel alloys for jet engines, high-quality knives, and tools. Write a balanced chemical equation for this process. What mass of calcium is needed, in theory, to produce 20.0 kg of vanadium from vanadium(V) oxide?

61. Galvanized steel consists of steel with a thin coating of zinc to reduce corrosion. The zinc can be deposited electrolytically, by making the steel object the cathode and a block of zinc the anode in an electrochemical cell containing a dissolved zinc salt. Suppose a steel garbage can is to be galvanized and requires that a total mass of 7.32 g of zinc be coated to the required thickness. How long should a current of 8.50 A be passed through the cell to achieve this?

62. In the electroplating of a silver spoon, the spoon acts as the cathode and a piece of pure silver as the anode. Both dip into a solution of silver cyanide (AgCN). Suppose that a current of 1.5 A is passed through such a cell for 22 minutes and that the spoon has a surface area of 16 cm^2. Calculate the average thickness of the silver layer deposited on the spoon, taking the density of silver to be 10.5 g cm^{-3}.

A DEEPER LOOK . . . Electrolysis of Water and Aqueous Solutions

63. An electrolytic cell consists of a pair of inert metallic electrodes in a solution buffered to pH = 5.0 and containing nickel sulfate ($NiSO_4$) at a concentration of 1.00 M. A current of 2.00 A is passed through the cell for 10.0 hours.

(a) What product is formed at the cathode?

(b) What is the mass of this product?

(c) If the pH is changed to pH = 1.0, what product will form at the cathode?

64. A 0.100 M neutral aqueous $CaCl_2$ solution is electrolyzed using platinum electrodes. A current of 1.50 A passes through the solution for 50.0 hours.

(a) Write the half-reactions occurring at the anode and at the cathode.
(b) What is the decomposition potential?
(c) Calculate the mass, in grams, of the product formed at the cathode.

ADDITIONAL PROBLEMS

65. The drain cleaner Drano consists of aluminum turnings mixed with sodium hydroxide. When it is added to water, the sodium hydroxide dissolves and releases heat. The aluminum reacts with water to generate bubbles of hydrogen and aqueous ions. Write a balanced net ionic equation for this reaction.

66. Sulfur-containing compounds in the air tarnish silver, giving black Ag_2S. A practical method of cleaning tarnished silverware is to place the tarnished item in electrical contact with a piece of zinc and dip both into water containing a small amount of salt. Write balanced half-equations to represent what takes place.

67. A current passed through inert electrodes immersed in an aqueous solution of sodium chloride produces chlorate ion, $ClO_3^-(aq)$, at the anode and gaseous hydrogen at the cathode. Given this fact, write a balanced equation for the chemical reaction if gaseous hydrogen and aqueous sodium chlorate are mixed and allowed to react spontaneously until they reach equilibrium.

68. A galvanic cell is constructed by linking a $Co^{2+}|Co(s)$ half-cell to an $Ag^+|Ag(s)$ half-cell through a salt bridge and then connecting the cobalt and silver electrodes through an external circuit. When the circuit is closed, the cell voltage is measured to be 1.08 V and silver is seen to plate out while cobalt dissolves.

(a) Write the half-reactions that occur at the anode and at the cathode and the balanced overall cell reaction.
(b) The cobalt electrode is weighed after 150 minutes of operation and is found to have decreased in mass by 0.36 g. By what amount has the silver electrode increased in mass?
(c) What is the average current drawn from the cell during this period?

69. The galvanic cell $Zn(s)|Zn^{2+}(aq)||Ni^{2+}(aq)|Ni(s)$ is constructed using a completely immersed zinc electrode that weighs 32.68 g and a nickel electrode immersed in 575 mL of 1.00 M $Ni^{2+}(aq)$ solution. A steady current of 0.0715 A is drawn from the cell as the electrons move from the zinc electrode to the nickel electrode.

(a) Which reactant is the limiting reactant in this cell?
(b) How long does it take for the cell to be completely discharged?
(c) How much mass has the nickel electrode gained when the cell is completely discharged?
(d) What is the concentration of the $Ni^{2+}(aq)$ when the cell is completely discharged?

70. A newly discovered bacterium can reduce selenate ion, $SeO_4^{2-}(aq)$, to elemental selenium, Se(*s*), in reservoirs. This is significant because the soluble selenate ion is potentially toxic, but elemental selenium is insoluble and harmless. Assume that water is oxidized to oxygen as the selenate ion is reduced. Compute the mass of oxygen produced if all the selenate in a 10^{12}-L reservoir contaminated with 100 mg L^{-1} of selenate ion is reduced to selenium.

71. Thomas Edison invented an electric meter that was nothing more than a simple coulometer, a device to measure the amount of electricity passing through a circuit. In this meter, a small, fixed fraction of the total current supplied to a household was passed through an electrolytic cell, plating out zinc at the cathode. Each month the cathode could then be removed and weighed to determine the amount of electricity used. If 0.25% of a household's electricity passed through such a coulometer and the cathode increased in mass by 1.83 g in a month, how many coulombs of electricity were used during that month?

72. The chief chemist of the Brite-Metal Electroplating Co. is required to certify that the rinse solutions that are discharged from the company's tin-plating process into the municipal sewer system contain no more than 10 ppm (parts per million) by mass of Sn^{2+}. The chemist devises the following analytical procedure to determine the concentration. At regular intervals, a 100-mL (100-g) sample is withdrawn from the waste stream and acidified to pH = 1.0. A starch solution and 10 mL of 0.10 M potassium iodide are added, and a 25.0-mA current is passed through the solution between platinum electrodes. Iodine appears as a product of electrolysis at the anode when the oxidation of Sn^{2+} to Sn^{4+} is practically complete and signals its presence with the deep blue color of a complex formed with starch. What is the maximum duration of electrolysis to the appearance of the blue color that ensures that the concentration of Sn^{2+} does not exceed 10 ppm?

73. Estimate the cost of the electrical energy needed to produce 1.5×10^{10} kg (a year's supply for the world) of aluminum from $Al_2O_3(s)$ if electrical energy costs 10 cents per kilowatt-hour (1 kWh = 3.6 MJ = 3.6×10^6 J) and if the cell voltage is 5 V.

74. Titanium can be produced by electrolytic reduction from an anhydrous molten salt electrolyte that contains titanium(IV) chloride and a spectator salt that furnishes ions to make the electrolyte conduct electricity. The standard enthalpy of formation of $TiCl_4(\ell)$ is -750 kJ mol^{-1}, and the standard entropies of $TiCl_4(\ell)$, $Ti(s)$, and $Cl_2(g)$ are 253, 30, and 223 J K^{-1} mol^{-1}, respectively. What minimum applied voltage will be necessary at 100°C?

75. A half-cell has a graphite electrode immersed in an acidic solution (pH 0) of Mn^{2+} (concentration 1.00 M) in contact with solid MnO_2. A second half-cell has an acidic solution (pH 0) of H_2O_2 (concentration 1.00 M) in contact with a platinum electrode past which gaseous oxygen at a pressure of 1.00 atm is bubbled. The two half-cells are connected to form a galvanic cell.

(a) By referring to Appendix E, write balanced chemical equations for the half-reactions at the anode and the cathode and for the overall cell reaction.
(b) Calculate the cell voltage.

76. By considering these half-reactions and their standard reduction potentials,

$$Pt^{2} + 2\,e^- \longrightarrow Pt \qquad \mathcal{E}^\circ = 1.2\text{ V}$$

$$NO_3^- + 4\,H_3O^+ + 3\,e^- \longrightarrow NO + 6\,H_2O \qquad \mathcal{E}^\circ = 0.96\text{ V}$$

$$PtCl_4^{2-} + 2\,e^- \longrightarrow Pt + 4\,Cl^- \qquad \mathcal{E}^\circ = 0.73\text{ V}$$