

Finally, no work is done if there is no net change in the number of moles of gases from reactants to products.⁴

Enthalpy

In general, for a constant-pressure process we write

$$\begin{aligned}\Delta U &= q + w \\ &= q_P - P\Delta V\end{aligned}$$

or

$$q_P = \Delta U + P\Delta V \quad (7.9)$$

where the subscript “P” denotes constant-pressure conditions.

We now introduce a new thermodynamic function called **enthalpy** (*H*) which is defined by the equation

$$H = U + PV \quad (7.10)$$

where *U* is the internal energy of the system and *P* and *V* are the pressure and volume of the system, respectively. Because *U* and *PV* have units of energy, enthalpy also has units of energy. Furthermore, *U*, *P*, and *V* are all state functions, so the changes in (*U* + *PV*) depend only on their initial and final states. Therefore, enthalpy is also a state function and the change in *H* (that is, ΔH) depends only on the initial and final states.

For any process, the change in enthalpy according to Equation 7.10 is given by

$$\Delta H = \Delta U + \Delta(PV) \quad (7.11)$$

If the pressure is held constant, then

$$\Delta H = \Delta U + P\Delta V \quad (7.12)$$

Comparing Equation 7.11 with Equation 7.9, we see that for a constant-pressure process,

$$q_P = \Delta H \quad (\text{constant pressure, expansion work only}) \quad (7.13)$$

Although *q* is not a state function, the heat change at constant pressure is equal to *H* because the “path” is defined and therefore it can have only a specific value.

We now have two quantities— ΔU and ΔH —that can be associated with a reaction. If the reaction occurs under constant-volume conditions, then the heat change, q_V , is equal to ΔU . When the reaction is carried out at constant pressure, though, the heat change, q_P , is equal to ΔH .

For a fixed sample of ideal gases, both *U* and *PV* depend only on temperature. As a result, the enthalpy of the gas (calculated using Equation 7.10) will also depend only upon temperature. Like changes in internal energy (Equation 7.5), the change in enthalpy for an ideal gas undergoing an isothermal process is identically zero:

$$\Delta H = 0 \quad (\text{ideal gas, isothermal process}) \quad (7.14)$$

4. This statement is only strictly true for gases behaving ideally because the molar volume of an ideal gas at a given pressure and temperature is the same for reactant and product gases. For real gases (and liquids and solids), the molar volume of reactant and product species will vary due to interparticle interactions and the volume of the system may change even if the number of reactant and product molecules in the reaction are equal. However, volume changes (and the subsequent work done) in such situations are generally quite small and can often be neglected.

Enthalpy of Reaction

Because most reactions occur under constant-pressure conditions, we can equate the heat change in these cases with the change in enthalpy. For any reaction of the type



the change in enthalpy, called the *enthalpy of reaction* (ΔH), is *the difference between the enthalpies of the products and the enthalpies of the reactants*:

$$\Delta H = H(\text{products}) - H(\text{reactants}) \quad (7.15)$$

The enthalpy of reaction can be positive or negative, depending on the process. For an *endothermic* reaction (where heat is absorbed by the system from the surroundings), ΔH is positive (that is, $\Delta H > 0$). For an *exothermic* reaction (where heat is released by the system to the surroundings), ΔH is negative (that is, $\Delta H < 0$).

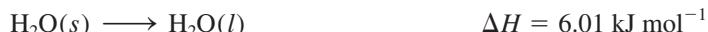
The change in enthalpy for a reaction is analogous to the change in the balance of your bank account as you make deposits and withdrawals. After a transaction (deposit or withdrawal), the change in your bank balance, ΔX , is given by

$$\Delta X = X_f - X_i$$

where X_i and X_f represent the initial and final bank balances, respectively. If your initial balance is \$100 and you deposit \$80 into your account, then $\Delta X = \$180 - \$100 = \$80$. A deposit corresponds, therefore, to an endothermic reaction. (The balance increases and so does the enthalpy of the system.) On the other hand, a withdrawal of \$60 means $\Delta X = \$40 - \$100 = -\$60$. The negative sign for ΔX means your account balance has decreased. Similarly, a negative value of ΔH reflects a decrease in enthalpy of the system as a result of an exothermic process. The difference between this analogy and Equation 7.15 is that, while you always know your exact bank balance, there is no way to know the enthalpies of individual products and reactants. In practice, we can only measure the *difference* in their values. Now let us apply the idea of enthalpy changes to two common processes, the first involving a physical change, the second a chemical change.

Thermochemical Equations

At 0°C and a pressure of 1 atm, ice melts to form liquid water. Measurements show that for every mole of ice converted to liquid water under these conditions, 6.01 kJ of heat energy are absorbed by the system (the ice). Because the pressure is constant, the heat change is equal to the enthalpy change, ΔH . Furthermore, this is an endothermic process ($\Delta H > 0$) because the ice must absorb energy to melt [Figure 7.9(a)]. The equation for this physical change is

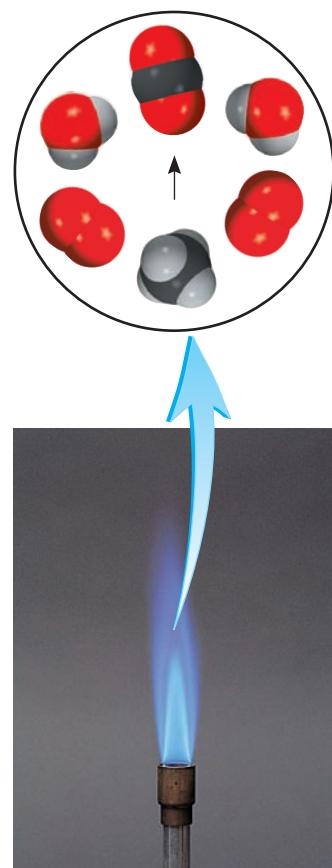


The value of ΔH is *per mole of the reaction (or process) as it is written*—that is, when 1 mole of ice is converted to 1 mole of liquid water.

The combustion of methane (CH_4), the principal component of natural gas, is an exothermic process ($\Delta H < 0$) because it releases heat to the surroundings:

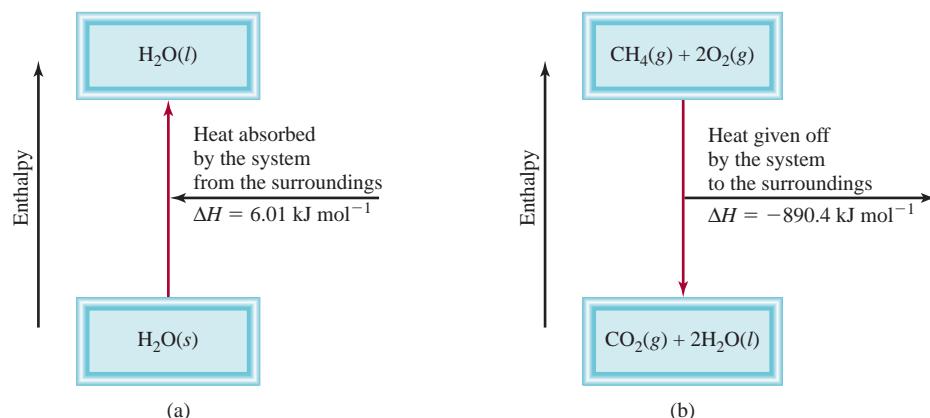


Under constant-pressure conditions this heat change is equal to the enthalpy change [Figure 7.9(b)]. The value of ΔH given in the balanced chemical equation means that



Methane gas burning from a Bunsen burner.

Figure 7.9 (a) Melting 1 mole of ice at 0°C (an endothermic process) results in an enthalpy increase in the system of 6.01 kJ. (b) Burning 1 mole of methane in oxygen gas (an exothermic process) results in an enthalpy decrease in the system of 890.4 kJ.



890.4 kJ of heat are released when 1 mole of CH_4 reacts with 2 moles of O_2 to yield 1 mole of CO_2 and 2 moles of liquid H_2O .

The equations for the melting of ice and the combustion of methane are called **thermochemical equations** because they *show the enthalpy changes as well as the molar relationships*. A correct thermochemical equation is always balanced, and the enthalpy change is always specified on a per-mole basis. The following guidelines are helpful in writing and interpreting thermochemical equations:

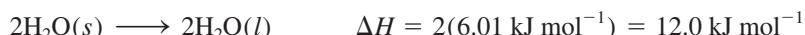
1. Always specify the physical states of all reactants and products in a thermochemical equation because they affect the enthalpy changes. In the combustion of methane, for example, if we specify water vapor rather than liquid water as a product,



the enthalpy change is $-802.4 \text{ kJ mol}^{-1}$ rather than $-890.4 \text{ kJ mol}^{-1}$, because 88.0 kJ are needed to convert 2 moles of liquid water to water vapor:

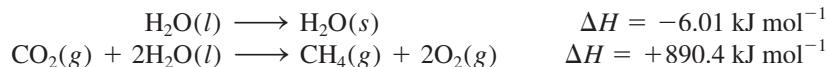


2. If we multiply or divide both sides of a thermochemical equation by a factor n , then ΔH must also change by the same factor. Thus, if $n = 2$ for the melting of ice, the resulting thermochemical equation is



The factor of 2 difference is necessary because enthalpy is an extensive quantity.

3. When we reverse a chemical equation, we change reactants to products and products to reactants. The magnitude of ΔH for the equation remains the same, but its sign changes. Thus, an endothermic reaction becomes exothermic and an exothermic reaction becomes endothermic, as shown by reversing the thermochemical equations for the melting of ice and the combustion of methane:



Example 7.3

During the manufacture of sulfuric acid, SO_2 is oxidized to SO_3 according to the following thermochemical equation:



Calculate the heat released when 74.6 g of SO_2 (molar mass = 64.07 g mol^{-1}) is converted to SO_3 under constant-pressure (1 bar) conditions.

Strategy Under constant-pressure conditions, the heat absorbed (q_P) per mole of a reaction is given by ΔH . According to the thermochemical equation, 99.1 kJ of heat is given off (note the negative sign) for every mole of SO_2 burned. To calculate the total amount of heat produced we first need to use the mass of SO_2 given in the problem statement and the molar mass of SO_2 to calculate the number of moles of SO_2 reacted.

Solution Beginning with the balanced thermochemical equation and 74.6 g of SO_2 , the amount of heat evolved can be calculated from the following sequence of conversions:



Therefore, the heat *absorbed* by the reaction is given by

$$q_P = 74.6 \text{ g } \text{SO}_2 \times \frac{1 \text{ mol } \text{SO}_2}{64.07 \text{ g } \text{SO}_2} \times \frac{-99.1 \text{ kJ}}{1 \text{ mol } \text{SO}_2} = -115 \text{ kJ}$$

The heat *released* by this exothermic reaction is then +115 kJ.

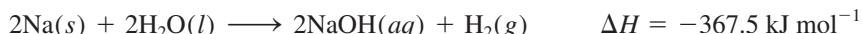
Check Because 74.6 g is greater than the molar mass of SO_2 , we expect the heat released to be larger than 99.1 kJ.

Practice Exercise Calculate the heat released when 266 g of white phosphorus (P_4) burns in air (at a constant pressure of 1 bar) according to the equation



A Comparison of ΔH and ΔU

What is the relationship between ΔH and ΔU for a process? To find out, consider the reaction between sodium metal and water:



According to this thermochemical equation, 2 moles of sodium react with 2 moles of water under constant-pressure conditions to produce 2 moles of aqueous NaOH, 1 mole of hydrogen gas, and 367.5 kJ of heat. Some of the energy produced by the reaction is used to do the work of pushing back a volume of air (V) against atmospheric pressure (P) (Figure 7.10), so the hydrogen gas can enter the atmosphere.

To calculate the change in internal energy, we rearrange Equation 7.11 as follows:

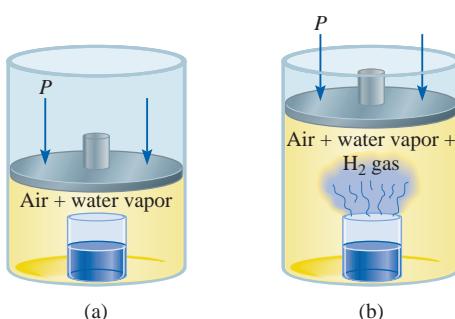
$$\Delta U = \Delta H - \Delta(PV)$$

If we assume the temperature is 25°C and ignore the small change in the volume of the solution, we can use the ideal gas equation to show that the volume of 1 mole of



Sodium reacting with water to form hydrogen gas.

Figure 7.10 (a) A beaker of water inside a cylinder fitted with a movable piston. The pressure inside is equal to the atmospheric pressure. (b) As the sodium metal reacts with water, hydrogen gas pushes the piston upward (doing work on the surroundings) until the pressure inside is again equal to that outside.



H_2 gas at 1.0 bar and 298 K is 24.8 L, so then $\Delta(PV) = 24.8 \text{ L bar}$ or 2.48 kJ. Finally,

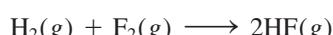
$$\Delta U = -367.5 \text{ kJ mol}^{-1} - 2.48 \text{ kJ mol}^{-1} = -370.0 \text{ kJ mol}^{-1}$$

Based on this calculation, ΔU and ΔH are approximately the same for this reaction. ΔH is slightly larger (less negative) than ΔU because some of the internal energy released is used to do gas expansion work, so less heat is evolved. For reactions that do not involve gases, ΔV is usually very small and so ΔU is practically the same as ΔH .

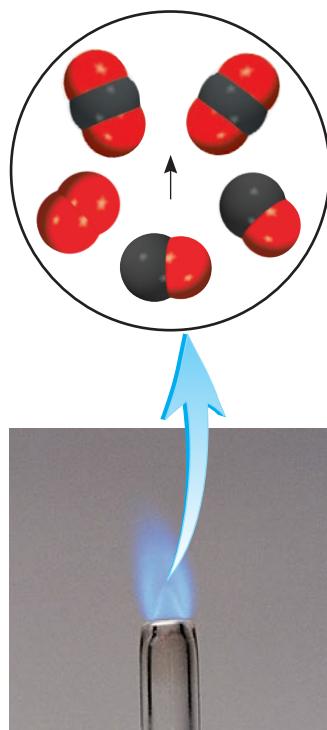
Another way to calculate the internal energy change of a gaseous reaction is to assume ideal gas behavior and constant temperature. In this case,

$$\begin{aligned}\Delta U &= \Delta H - \Delta(PV) \\ &= \Delta H - \Delta(nRT) \\ \Delta U &= \Delta H - RT\Delta n\end{aligned}\tag{7.16}$$

where Δn is defined as = number of moles of product gases – number of moles of reactant gases for one mole of reaction. Note that, if the number of moles of product gases and the number of moles of reactant gases are equal, as in the reaction



the difference between ΔU and ΔH will be very small because $\Delta n = 0$.



Carbon monoxide burns in air to form carbon dioxide.

Example 7.4

Calculate the change in internal energy when 2 moles of CO are converted to 2 moles of CO_2 at 1 bar and 25°C:



(Carbon monoxide in auto exhaust is the result of incomplete combusting of gasoline in the engine. The removal of this major pollutant from auto emissions by conversion to CO_2 via this reaction is one of the primary functions of catalytic converters in automobiles.)

Strategy We are given the molar enthalpy change, ΔH , for a reaction involving gases and are asked to calculate the change in molar internal energy, ΔU . Therefore, we need Equation 7.16. What is the change in the number of moles of gases? ΔH is given in kJ mol^{-1} , so what units should we use for R ?

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Solution According to the balanced chemical equation, 3 moles of gases are converted to 2 moles of gases, so

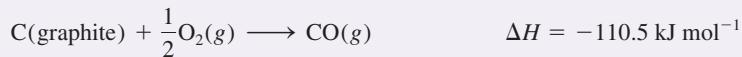
$$\begin{aligned}\Delta n &= \text{number of moles of product gas} - \text{number of moles of reactant gases} \\ &= 2 - 3 = -1\end{aligned}$$

Using $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and $T = 298 \text{ K}$ in Equation 7.16, we write

$$\begin{aligned}\Delta U &= \Delta H - RT\Delta n \\ &= -566.0 \text{ kJ mol}^{-1} - (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) (298 \text{ K})(-1 \text{ mol}) \\ &= -563.0 \text{ kJ mol}^{-1}\end{aligned}$$

Check The reacting gaseous system undergoes a compression (3 moles to 2 moles), so $\Delta V < 0$. Because $\Delta U = \Delta H - P \Delta V$ and ΔV is negative, we expect $\Delta U > \Delta H$, in agreement with our result.

Practice Exercise What is ΔU for the formation of 1 mole of CO from graphite at 1 bar and 25°C?



7.3 | The Temperature Change of a System Upon Heating Is Governed by Its Heat Capacity

When energy in the form of heat is added to any material, the temperature of the material rises.⁵ However, the amount of this temperature rise per unit of input heat energy depends both upon the material and the nature of the process.

Heat Capacities

For any heating process, adding an amount of energy in the form of heat (q) results in a temperature rise (ΔT) that is given by

$$q = C \Delta T \quad (7.17)$$

or

$$C = \frac{q}{\Delta T} \quad (7.18)$$

where the proportionality constant, C , is called the **heat capacity**, and is usually given in units of J K^{-1} . The heat capacity depends on the physical properties of the material, the amount of material present, and the precise nature of the process. Heat capacity is an extensive quantity, so doubling the size of a system also doubles the heat capacity. The **molar heat capacity** (\bar{C}) is the heat capacity per 1 mole of substance

$$\bar{C} = \frac{C}{n} = \frac{q}{n \Delta T} \quad (7.19)$$

5. This is true assuming that no phase transitions are occurring in the system. As we will see in Section 7.6, when heat is added to a system at a phase transition temperature (boiling point, freezing point, etc.), the temperature remains fixed as all the heat is used to convert one phase of the system into another.

Table 7.1

The Specific Heat Capacities of Some Common Substances at 25°C.

| Substance | Specific Heat (J g ⁻¹ °C ⁻¹) |
|---|--|
| Al | 0.900 |
| Au | 0.129 |
| C (graphite) | 0.720 |
| C (diamond) | 0.502 |
| Cu | 0.385 |
| Fe | 0.444 |
| Hg | 0.139 |
| H ₂ O | 4.184 |
| C ₂ H ₅ OH (ethanol) | 2.46 |

where n is the number of moles of substance. The **specific heat capacity** (C_s) is the heat capacity per 1 gram of substance:

$$C_s = \frac{C}{m} = \frac{q}{m\Delta T} \quad (7.20)$$

where m is the mass (in grams) of the substance. The specific heat capacities for several substances are listed in Table 7.1. The molar and specific heat capacities are both intensive properties and have units of J mol⁻¹ K⁻¹ and J g⁻¹ K⁻¹, respectively.

Unlike energy or enthalpy, the heat capacity of a system can be directly measured. From Equation 7.19, we can readily calculate the value of \bar{C} by adding a known amount of energy in the form of heat to a given amount of substance and measuring the temperature rise. However, the precise value of \bar{C} that we determine also depends upon how the heating process is performed. Although many different conditions can be realized in practice, we shall consider only the two most commonly encountered cases here: constant volume and constant pressure. If the substance is heated at constant volume, then the heat capacity determined using Equation 7.19 is called the **constant-volume heat capacity** (C_V). Similarly, C_P denotes the **constant-pressure heat capacity**, which describes heating under constant-pressure conditions.

Recall from Section 7.1 that the heat energy absorbed by a system in a constant-volume process is equal to the change in internal energy (that is, $\Delta U = q_V$). Hence, the constant-volume heat capacity is given by

$$C_V = \frac{q_V}{\Delta T} = \frac{\Delta U}{\Delta T} \quad (7.21)$$

or

$$\Delta U = C_V \Delta T = n \bar{C}_V \Delta T \quad (\text{constant } V \text{ process}) \quad (7.22)$$

Similarly, the heat energy absorbed by a system in a constant-pressure process is equal to the change in enthalpy—that is, $\Delta H = q_P$ (Equation 7.13). Hence, the constant-pressure heat capacity is given by

$$C_P = \frac{q_P}{\Delta T} = \frac{\Delta H}{\Delta T} \quad (7.23)$$

or

$$\Delta H = C_P \Delta T = n \bar{C}_P \Delta T \quad (\text{constant } P \text{ process}) \quad (7.24)$$

Equations 7.22 and 7.24 are valid as long as the heat capacities can be assumed to be independent of temperature, which is often a good approximation if the temperature change is small, say 50 K or less. For calculations in which the temperature dependence of the heat capacity cannot be ignored, we must use the differential forms of Equations 7.22 and 7.24:

$$dU = C_V dT \quad (7.25)$$

and

$$dH = C_P dT \quad (7.26)$$

which when integrated give

$$\Delta U = \int_{T_1}^{T_2} C_V dT \quad (7.27)$$

and

$$\Delta H = \int_{T_1}^{T_2} C_P dT \quad (7.28)$$

respectively. Studies of the temperature dependence of heat capacity for many substances show that it can be well approximated by an equation $C_p = a + bT$, where a and b are constants for a given substance over a particular temperature range. A similar equation also holds for C_V . For the special case of ideal gases, Equations 7.22, 7.24, 7.27, and 7.28 can be used for any process (constant P , constant V , etc.) because both the energy and enthalpy of ideal gases depend only on temperature (Equations 7.5 and 7.14).

In general, C_V and C_P are not equal to each other. In a constant-volume process the expansion work is zero (because $\Delta V = 0$) and all energy goes into changing the temperature of the system. However, heating at constant pressure leads, in most systems, to an expansion of the system ($\Delta V > 0$), so some of the energy input must be used to do work on the surroundings. Therefore, it takes more energy to increase the temperature of a system at constant pressure than at constant volume and we have $C_p > C_V$. For gases, the difference between C_p and C_V is significant because the change in volume on heating can be significant. For solids and liquids, however, the volume change is quite small, so C_p and C_V can usually be assumed to be identical.

For ideal gases, the difference between C_p and C_V can be determined. From the definition of enthalpy (Equation 7.10) we have

$$H = U + PV = U + nRT$$

where we have used the ideal gas equation ($PV = nRT$). For a given change in temperature, ΔT , the change in enthalpy for a fixed amount of ideal gas (n moles) is then

$$\begin{aligned}\Delta H &= \Delta U + \Delta(nRT) \\ &= \Delta U + nR\Delta T\end{aligned}$$

Substituting $\Delta U = C_V \Delta T$ (Equation 7.22) and $\Delta H = C_p \Delta T$ into the preceding equation gives

$$C_p \Delta T = C_V \Delta T + nR\Delta T$$

Dividing by ΔT and rearranging gives

$$C_p - C_V = nR$$

or

$$\bar{C}_p - \bar{C}_V = R \quad (\text{for an ideal gas}) \quad (7.29)$$

Therefore, for an ideal gas, the constant-pressure molar heat capacity always exceeds the constant-volume molar heat capacity by exactly R . The values of \bar{C}_p for many substances are given in Appendix 2.

Example 7.5

Calculate ΔU and ΔH for heating of 35.36 g of krypton ($\bar{C}_V = 12.47 \text{ J mol}^{-1} \text{ K}^{-1}$) from 300 K to 400 K. Assume ideal gas behavior and that the heat capacities at constant volume and constant pressure are independent of temperature.

Strategy Because we assume that the heat capacities are independent of temperature, we can use Equations 7.22 and 7.24 to calculate ΔH and ΔU , but to do so we need both \bar{C}_V (which is given) and \bar{C}_P . It is an ideal gas, so we only need \bar{C}_V because \bar{C}_P can be obtained using Equation 7.29. Note that, because both the energy and enthalpy for ideal gases depend only upon temperature, it is not necessary to know the exact nature of the heating process (constant P , constant V , etc.) to apply Equations 7.22 and 7.24.

Solution The quantity 35.36 g of Kr corresponds to $35.36 \text{ g}/83.80 \text{ g mol}^{-1} = 0.4219 \text{ mol}$. Thus, from Equation 7.21 we have

$$\begin{aligned}\Delta U &= n\bar{C}_V\Delta T \\ &= (0.4219 \text{ mol})(12.47 \text{ J mol}^{-1} \text{ K}^{-1})(400 \text{ K} - 300 \text{ K}) \\ &= 526 \text{ J}\end{aligned}$$

For ΔH we need \bar{C}_P , which from Equation 7.29 is

$$\bar{C}_P = \bar{C}_V + R = 12.47 \text{ J mol}^{-1} \text{ K}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 20.79 \text{ J mol}^{-1} \text{ K}^{-1}$$

so using Equation 7.24 gives

$$\begin{aligned}\Delta H &= n\bar{C}_P\Delta T \\ &= (0.4219 \text{ mol})(20.79 \text{ J mol}^{-1} \text{ K}^{-1})(400 \text{ K} - 300 \text{ K}) \\ &= 877 \text{ J}\end{aligned}$$

Check The answer is consistent with the fact that the enthalpy change on heating should be larger than energy change because $\bar{C}_P > \bar{C}_V$.

Practice Exercise: A quantity of 10.0 L of carbon dioxide (CO_2) gas, initially at a pressure of 1.00 bar, is heated from 250 K to 300 K. Calculate the values of ΔH and ΔU for this process. Assume ideal-gas behavior and that the heat capacities at constant volume and constant pressure are independent of temperature. For carbon dioxide, $\bar{C}_V = 28.80 \text{ J mol}^{-1} \text{ K}^{-1}$.

Calorimetry

In the laboratory, heat changes in physical and chemical processes are measured with a *calorimeter*, a closed container designed specifically for this purpose. Such experimental studies are called *calorimetry*, which *the measurement of heat changes for processes*.

Constant-Volume Calorimetry

The heat of a reaction, such as combustion, is usually measured by placing a known mass of a compound in a steel container called a *constant-volume bomb calorimeter*. The calorimeter is then filled with oxygen at about 30 bar of pressure. The closed bomb is immersed in a known amount of water, as shown in Figure 7.11. The sample is ignited electrically, and the heat produced by the combustion reaction can be calculated accurately by recording the rise in temperature of the water. The heat given off by the sample is absorbed by the water and the bomb. The special design of the

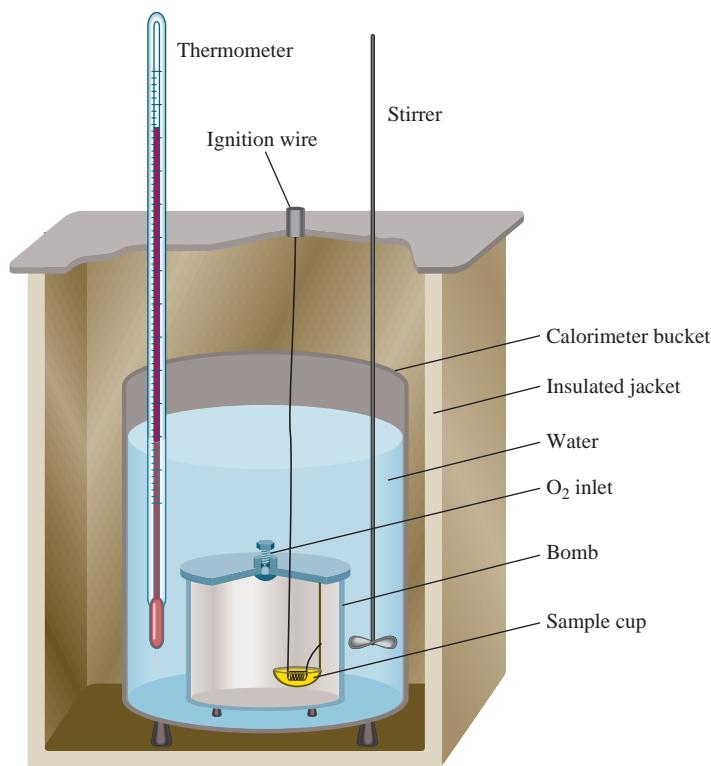


Figure 7.11 A constant-volume bomb calorimeter. The bomb is filled with oxygen gas before it is placed in the bucket. The sample is ignited electrically, and the heat produced by the reaction can be accurately determined by measuring the temperature increase in the known amount of surrounding water.

calorimeter enables us to assume that no heat (or mass) is lost to the surroundings during the time it takes to make measurements. Therefore, we can call the bomb and the water in which it is submerged an isolated system. Because no heat enters or leaves the system throughout the process, the heat change of the system (q_{system}) must be zero and we can write

$$q_{\text{system}} = q_{\text{cal}} + q_{\text{rxn}} = 0 \quad (7.30)$$

where q_{cal} and q_{rxn} are the heat changes for the calorimeter and the reaction, respectively. Thus,

$$q_{\text{rxn}} = -q_{\text{cal}} \quad (7.31)$$

To calculate q_{cal} , we need to know the heat capacity of the calorimeter (C_{cal}) and the temperature rise, that is,

$$q_{\text{cal}} = C_{\text{cal}} \Delta T \quad (7.32)$$

The quantity C_{cal} is calibrated by burning a substance with an accurately known heat of combustion. For example, it is known that the combustion of 1 g of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) releases 26.42 kJ of heat. If the temperature rise is 4.673°C , then the heat capacity of the calorimeter is given by

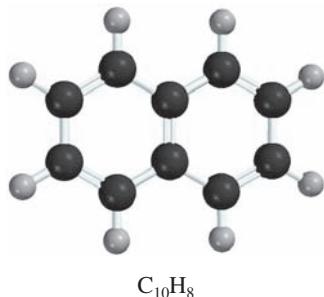
$$\begin{aligned} C_{\text{cal}} &= \frac{q_{\text{cal}}}{\Delta T} \\ &= \frac{26.42 \text{ J}}{4.673^\circ\text{C}} = 5.654 \text{ kJ } ^\circ\text{C}^{-1} \end{aligned}$$

Once C_{cal} has been determined, the calorimeter can be used to measure the heat of combustion of other substances.

Note that because reactions in a bomb calorimeter occur under constant-volume rather than constant-pressure conditions, the heat changes *do not* correspond to the enthalpy change ΔH (see Section 7.2). It is possible to correct the measured heat changes so that they correspond to H values, but the corrections usually are quite small so we will not concern ourselves with the details here. Finally, it is interesting to note that the energy contents of food and fuel (usually expressed in calories where 1 cal = 4.184 J) are measured with constant-volume calorimeters. (See the inset on page 390.)

Example 7.6

A quantity of 1.435 g of naphthalene (C_{10}H_8), a pungent-smelling substance used in moth repellents, was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose from 20.28°C to 25.95°C . If the heat capacity of the bomb plus water was $10.17 \text{ kJ } ^\circ\text{C}^{-1}$, calculate the heat of combustion of naphthalene on a molar basis, that is, find the molar heat of combustion.



Strategy Knowing the heat capacity and the temperature rise, we can use Equation 7.32 to calculate the heat absorbed by the calorimeter. This gives us the heat generated by the combustion of 1.435 g of naphthalene, which must be converted to molar heat of combustion using the molar mass of naphthalene.

Solution The heat absorbed by the bomb and water is equal to the product of the heat capacity and the temperature change. From Equation 7.32, assuming no heat is lost to the surroundings, we write

$$\begin{aligned} q_{\text{cal}} &= C_{\text{cal}} \Delta T \\ &= (10.17 \text{ kJ } ^\circ\text{C}^{-1})(25.95^\circ\text{C} - 20.28^\circ\text{C}) \\ &= 57.66 \text{ kJ} \end{aligned}$$

Because $q_{\text{sys}} = q_{\text{cal}} - q_{\text{rxn}} = 0$, $q_{\text{cal}} = -q_{\text{rxn}}$. The heat change of the reaction is -57.66 kJ . This is the heat released by the combustion of 1.435 g of C_{10}H_8 ; therefore, we can write the conversion factor as

$$\frac{-57.66 \text{ kJ}}{1.435 \text{ g } \text{C}_{10}\text{H}_8}$$

The molar mass of naphthalene is 128.2 g, so the heat of combustion of 1 mole of naphthalene is

$$\begin{aligned} \text{molar heat of combustion} &= \frac{-57.66 \text{ kJ}}{1.435 \text{ g } \text{C}_{10}\text{H}_8} \times \frac{128.2 \text{ g } \text{C}_{10}\text{H}_8}{1 \text{ mol } \text{C}_{10}\text{H}_8} \\ &= -5.151 \times 10^3 \text{ kJ mol}^{-1} \end{aligned}$$

Check Knowing that the combustion reaction is exothermic and that the molar mass of naphthalene is much greater than 1.4 g, is the answer reasonable? Under the reaction conditions, can the heat change (-57.66 kJ) be equated to the enthalpy change of the reaction?

Practice Exercise A quantity of 1.922 g of methanol (CH_3OH) was burned in a constant-volume bomb calorimeter. Consequently, the temperature of the water rose by 4.20°C . If the heat capacity of the bomb plus water was $10.4 \text{ kJ } ^\circ\text{C}^{-1}$, calculate the molar heat of combustion of methanol.

Constant-Pressure Calorimetry

A simpler device than the constant-volume calorimeter is the constant-pressure calorimeter, which is used to determine the heat changes for noncombustion reactions. A crude constant-pressure calorimeter can be constructed from two Styrofoam coffee cups, as shown in Figure 7.12. This device measures the heat effects of a variety of reactions, such as acid-base neutralization, as well as the heat of solution and heat of dilution.

Because the pressure is constant, the heat change for the process (q_{rxn}) is equal to the enthalpy change (ΔH). As in the case of a constant-volume calorimeter, we treat the calorimeter as an isolated system. Furthermore, we neglect the small heat capacity of the coffee cups in our calculations. Table 7.2 lists some reactions that have been studied with the constant-pressure calorimeter.

Example 7.7

A lead pellet having a mass of 26.47 g at 89.98°C was placed in a constant-pressure calorimeter of negligible heat capacity containing 100.0 mL of water. The water temperature rose from 22.50°C to 23.17°C. What is the specific heat capacity of the lead pellet?

Strategy We know the masses of water and the lead pellet as well as the initial and final temperatures. Assuming no heat is lost to the surroundings, we can equate the heat lost by the lead pellet to the heat gained by the water. Knowing the specific heat of water, we can then calculate the specific heat of lead.

Solution Treating the calorimeter as an isolated system (no heat lost to the surroundings), we write

$$q_{\text{Pb}} + q_{\text{H}_2\text{O}} = 0$$

or

$$q_{\text{Pb}} = -q_{\text{H}_2\text{O}}$$

The heat gained by the water is given by

$$q_{\text{H}_2\text{O}} = mC_s \Delta t$$

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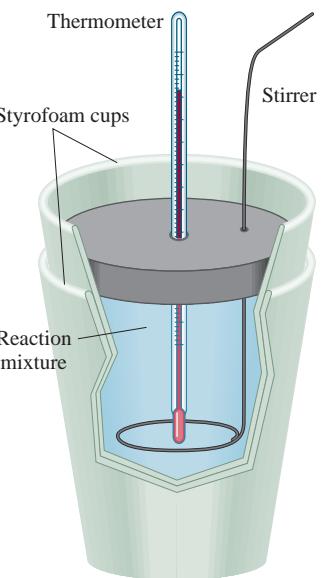


Figure 7.12 A constant-pressure calorimeter made of two Styrofoam coffee cups. The outer cup helps to insulate the reacting mixture from the surroundings. Two solutions of known volume containing the reactants at the same temperature are carefully mixed in the calorimeter. The heat produced or absorbed by the reaction can be determined by measuring the temperature change.

Table 7.2 Heats of Some Typical Reactions Measured at 25°C and Constant Pressure

| Type of Reaction | Example | ΔH (kJ mol ⁻¹) |
|------------------------|--|------------------------------------|
| Heat of neutralization | $\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$ | -56.2 |
| Heat of ionization | $\text{H}_2\text{O}(l) \longrightarrow \text{H}^+(aq) + \text{OH}^-(aq)$ | 56.2 |
| Heat of fusion | $\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$ | 6.01 |
| Heat of vaporization | $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$ | 44.0* |
| Heat of reaction | $\text{MgCl}_2(s) + 2\text{Na}(l) \longrightarrow 2\text{NaCl}(s) + \text{Mg}(s)$ | -180.2 |

*Measured at 25°C. At 100°C, the value is 40.79 kJ.

Continued—

where m and C_s are the mass and specific heat capacity, respectively, and $\Delta t = t_f - t_i$. Therefore,

$$\begin{aligned} q_{\text{H}_2\text{O}} &= (100.0 \text{ g})(4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1})(23.17^{\circ}\text{C} - 22.50^{\circ}\text{C}) \\ &= 280.3 \text{ J} \end{aligned}$$

Because the heat lost by the lead pellet is equal to the heat gained by the water, so $q_{\text{Pb}} = -280.3 \text{ J}$. To determine the specific heat of Pb, we write

$$q_{\text{Pb}} = mC_s \Delta t$$

which gives, after rearrangement

$$\begin{aligned} C_s &= \frac{q_{\text{Pb}}}{m \Delta t} \\ &= \frac{-280.3 \text{ J}}{(26.47 \text{ g})(23.17^{\circ}\text{C} - 89.98^{\circ}\text{C})} \\ &= 0.158 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1} \end{aligned}$$

Practice Exercise A 30.14-g stainless steel ball bearing at 117.82°C is placed in a constant-pressure calorimeter containing 120.0 mL of water at 18.44°C . If the specific heat of the ball bearing is $0.474 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$, calculate the final temperature of the water. Assume the calorimeter to have negligible heat capacity.

Example 7.8

A quantity of $1.00 \times 10^2 \text{ mL}$ of 0.500 M HCl was mixed with $1.00 \times 10^2 \text{ mL}$ of 0.500 M NaOH in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and NaOH solutions was the same, 22.50°C , and the final temperature of the mixed solution was 25.86°C . Calculate the heat change for the neutralization reaction on a molar basis



Assume that the densities and specific heats of the solutions are the same as for water (1.00 g mL^{-1} and $4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$, respectively).

Strategy Because the temperature rose, the neutralization reaction is exothermic. Find the total mass of the solution and use Equation 7.20 to determine the heat absorbed given the specific heat. Determine the relationship between the heat absorbed by the solution and the heat of reaction.

Solution Assuming no heat is lost to the surroundings, $q_{\text{sys}} = q_{\text{soln}} + q_{\text{rxn}} = 0$, so $q_{\text{rxn}} = -q_{\text{soln}}$, where q_{soln} is the heat absorbed by the combined solution. Because the density of the solution is 1.00 g mL^{-1} , the mass of a 100-mL solution is 100 g. To find the heat absorbed by the solution given the specific heat, we use Equation 7.20:

$$\begin{aligned} q_{\text{soln}} &= mC_s \Delta T \\ &= (1.00 \times 10^2 \text{ g} + 1.00 \times 10^2 \text{ g})(4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1})(25.86^{\circ}\text{C} - 22.50^{\circ}\text{C}) \\ &= 2.81 \times 10^3 \text{ J} = 2.81 \text{ kJ} \end{aligned}$$

Because $q_{\text{rxn}} = -q_{\text{soln}}$, $q_{\text{rxn}} = -2.81 \text{ kJ}$.

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From the molarities given, the number of moles of both HCl and NaOH in 1.00×10^2 mL solution is

$$\frac{0.500 \text{ mol}}{1 \text{ L}} \times 0.100 \text{ L} = 0.0500 \text{ mol}$$

Therefore, the heat of neutralization when 1.00 mole of HCl reacts with 1.00 mole of NaOH is

$$\text{heat of neutralization} = \frac{-2.81 \text{ kJ}}{0.0500 \text{ mol}} = -56.2 \text{ kJ mol}^{-1}$$

Check Is the sign consistent with the nature of the reaction? Under the reaction condition, can the heat change be equated to the enthalpy change?

Practice Exercise A quantity of 4.00×10^2 mL of 0.600 M HNO₃ is mixed with 4.00×10^2 mL of 0.300 M Ba(OH)₂ in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of both solutions is the same at 18.46°C . What is the final temperature of the solution? (Use the density and specific heat data given in Example 7.8.)

The Molecular Interpretation of Heat Capacities

We defined heat as that part of the energy that is added to the multitudes of molecular variables that we do not explicitly observe in a system (the positions and velocities of individual molecules, for example). The way in which this energy is distributed can be understood in terms of a concept based on classical mechanics and directly applicable to gas behavior.

This concept, called the **equipartition of energy theorem**, states that the energy in a molecule is, on average, distributed evenly among all types of molecular motion (degrees of freedom). The number of degrees of freedom in a molecule is the number of variables that are required to describe its motion. For monatomic gases, we require three coordinates (x , y , and z) to completely define the position of each atom—we say that each atom possesses three translational degrees of freedom. For molecules, on the other hand, additional degrees of freedom are required to describe rotational and vibrational motion. The equipartition of energy theorem is a fundamental result from **statistical mechanics**, the study of the molecular origin of thermodynamics.

To see how the equipartition theorem works, first consider the simple case of a monatomic ideal gas (which would be a good model for argon or neon at low pressure). We saw in Section 5.4 that each of the N atoms in this system contributes $3/2 k_{\text{B}}T$ to the total translational kinetic energy (Equation 5.34), where k_{B} is Boltzmann's constant. Because the system is ideal and there are no interatomic interactions, the potential energy is zero and the total energy of the gas is

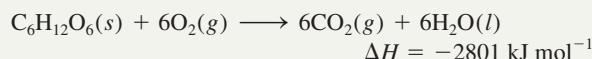
$$U(\text{monatomic}) = \frac{3}{2} N k_{\text{B}} T = \frac{3}{2} n R T \quad (7.33)$$

where we have used the fact that $R = N_A k_{\text{B}}$, where N_A is Avagadro's number. Thus, if we change the temperature by ΔT , the change in energy is given by

$$\Delta U = \frac{3}{2} N k_{\text{B}} \Delta T = \frac{3}{2} n R \Delta T \quad (7.34)$$

Fuel Values of Foods and Other Substances

The food we eat is broken down (metabolized) in stages by a group of complex biological molecules called *enzymes*. Most of the energy released at each stage is captured for function and growth. One interesting aspect of metabolism is that the overall change in energy is the same as it is in combustion. For example, the total enthalpy change for the conversion of glucose ($C_6H_{12}O_6$) to carbon dioxide and water is the same whether we burn the substance in air or digest it in our bodies:



The important difference between metabolism and combustion is that the latter is usually a one-step, high-temperature process. Consequently, much of the energy released by combustion is lost to the surroundings.

Various foods have different compositions and hence different energy contents. The energy content of food is generally measured in calories. The *calorie* (*cal*) is a non-SI unit of energy that is defined as the amount of energy required to heat 1 g of liquid water by 1°C and is equivalent to 4.184 J. In the context of nutrition, however, the calorie we speak of (sometimes called a *nutritional calorie* or “big calorie”) is actually equal to a *kilocalorie*, that is,

$$1 \text{ Cal} = 1000 \text{ cal} = 4184 \text{ J}$$

Note the use of a capital “C” to represent the “big calorie.” The bomb calorimeter described in Section 7.3 is ideally suited for measuring the energy content, or “fuel value,” of foods. Fuel values are just the enthalpies of combustion (see the table). In order to be analyzed in a bomb calorimeter, food must be dried first because most foods contain a considerable amount of water. Because the composition of particular foods is often not known, fuel values are expressed in terms of kJ g^{-1} rather than kJ mol^{-1} .

Fuel Values of Foods and Some Common Fuels

| Substance | $\Delta H_{\text{combustion}}$ (kJ g $^{-1}$) |
|-------------|--|
| Apple | -2 |
| Beef | -8 |
| Beer | -1.5 |
| Bread | -11 |
| Butter | -34 |
| Cheese | -18 |
| Eggs | -6 |
| Milk | -3 |
| Potatoes | -3 |
| Charcoal | -35 |
| Coal | -30 |
| Gasoline | -34 |
| Kerosene | -37 |
| Natural Gas | -50 |
| Wood | -20 |

Nutrition Facts

Serving Size 6 cookies (28g)
Servings Per Container about 11

| Amount Per Serving | |
|-------------------------------|-------------------------------|
| Calories | 120 Calories from Fat 30 |
| | % Daily Value* |
| Total Fat 4g | 6% |
| Saturated Fat 0.5g | 4% |
| Polyunsaturated Fat 0g | |
| Monounsaturated Fat 1g | |
| Cholesterol 5mg | 2% |
| Sodium 105mg | 4% |
| Total Carbohydrate 20g | 7% |
| Dietary Fiber Less than 1gram | 2% |
| Sugars 7g | |
| Protein 2g | |

The labels on food packages reveal the calorie content of the food inside.

Comparing Equations 7.34 and 7.22 yields

$$\bar{C}_V(\text{monatomic}) = \frac{3}{2}Nk_B = \frac{3}{2}nR \quad (7.35)$$

giving a molar constant-volume heat capacity

$$\bar{C}_V(\text{monatomic}) = \frac{3}{2}R = 12.471 \text{ J mol}^{-1} \text{ K}^{-1} \quad (7.36)$$

using $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. Each atom in this system has three translational degrees of freedom, so each translational degree of freedom contributes $1/2 k_B T$ to the total energy and $1/2 k$ to the constant volume heat capacity. On a molecular level, the heat capacity can be understood as *a measure of the number of degrees of freedom of a system available for the storage of energy*. The equipartition theorem also gives a useful alternative definition of temperature as *a measure of the amount of energy available, on average, in each molecular degree of freedom*.

The equipartition theorem prediction for the constant-pressure heat capacity \bar{C}_P of a monatomic ideal gas can be determined from \bar{C}_V (Equation 7.36) using the relationship between \bar{C}_P and \bar{C}_V given in Equation 7.29.

$$\bar{C}_P(\text{monatomic}) = \bar{C}_V + R = \frac{3}{2}R + R = \frac{5}{2}R = 20.785 \text{ J mol}^{-1} \text{ K}^{-1} \quad (7.37)$$

For molecules containing two or more atoms, other types of motion, such as rotation and vibration, are also present. For a molecule containing M atoms, we require $3M$ coordinates to describe the motion of every atom. Three coordinates are needed to describe the translational motion of the center of mass. The remaining $3M - 3$ coordinates are needed to describe rotation and vibration. For linear molecule, such as CO₂ or HCl, two angles are required to specify the orientation of the molecule relative to two coordinate axes through the center of mass and perpendicular to the bond axes—rotation about the bond axis leaves the molecule unchanged, so it does not constitute a degree of freedom. This leaves $(3M - 5)$ vibrational degrees of freedom for a linear molecule. For example, Figure 7.13 shows the translational, rotational, and vibrational motions of a diatomic molecule.

In contrast, three angles about three mutually perpendicular axes through the center of mass are needed to describe the rotation of a nonlinear molecule, such as H₂O or CH₄, leaving $(3M - 6)$ degrees of freedom for vibration.

The equipartition theorem states that the energy will be distributed equally among the degrees of freedom of the system; therefore, each rotational degree of freedom will contain the same amount of energy ($1/2 k_B T$) as each translational degree of freedom. Because the energy of molecular vibration consists of contributions from both kinetic energy (due to vibrational motion) and potential energy (due to bond stretching and compression), the equipartition theorem predicts that each vibrational degree of freedom will contribute $k_B T$ to the energy ($1/2 k_B T$) each from kinetic and

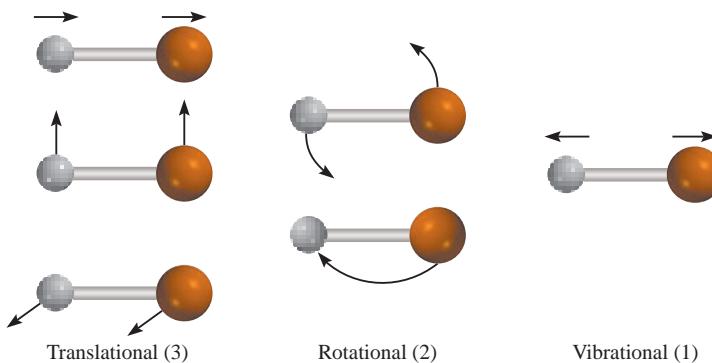


Figure 7.13 The three translational, two rotational, and one vibrational motions of a diatomic molecule, such as HCl.

Table 7.3 Equipartition Theorem Contributions to C_V for Ideal Gases

| Type of Molecule | Translation | Rotation | Vibration |
|--------------------|----------------|----------------|-------------|
| Atom | $\frac{3}{2}R$ | — | — |
| Linear Molecule | $\frac{3}{2}R$ | R | $(3M - 5)R$ |
| Nonlinear Molecule | $\frac{3}{2}R$ | $\frac{3}{2}R$ | $(3M - 6)R$ |

potential energy). Thus, for an ideal gas containing n moles of nonlinear molecules, the equipartition theorem gives an energy of

$$U(\text{nonlinear}) = \left[\underbrace{\frac{3}{2}}_{\text{translational}} + \underbrace{\frac{3}{2}}_{\text{rotational}} + \underbrace{(3M - 6)}_{\text{vibrational}} \right] nRT \quad (7.38)$$

corresponding to a molar constant-volume heat capacity of

$$\bar{C}_V(\text{nonlinear}) = \left[\underbrace{\frac{3}{2}}_{\text{translational}} + \underbrace{\frac{3}{2}}_{\text{rotational}} + \underbrace{(3M - 6)}_{\text{vibrational}} \right] R \quad (7.39)$$

For a linear molecule, we have

$$C_V(\text{linear}) = \left[\underbrace{\frac{3}{2}}_{\text{translational}} + \underbrace{\frac{2}{2}}_{\text{rotational}} + \underbrace{(3M - 5)}_{\text{vibrational}} \right] R \quad (7.40)$$

The contributions to \bar{C}_V by the translational, rotational, and vibrational degrees of freedom for ideal gases of atoms, linear molecules, and nonlinear molecules are summarized in Table 7.3.

The values of \bar{C}_P for nonlinear and linear molecules can be obtained by adding R to the C_V values in Equations 7.39 and 7.40, respectively.

In Table 7.4, we compare, for a number of gases, the values \bar{C}_P predicted from the equipartition theorem with experimentally measured heat capacities. For monoatomic gases the agreement between experiment and theory is excellent; however, considerable deviations are observed for molecular gases. To understand the origin of these discrepancies, consider diatomic hydrogen (H_2). For a diatomic molecule, $M = 2$ and Equation 7.40, together with Equation 7.29 ($\bar{C}_P = C_V + R$), yields

$$\bar{C}_P(\text{diatomic}) = \left[\underbrace{\frac{3}{2}}_{\text{translational}} + \underbrace{1}_{\text{rotational}} + \underbrace{1}_{\text{vibrational}} \right] R + R = \frac{9}{2}R = 37.41 \text{ J mol}^{-1} \text{ K}^{-1}$$

However, from Table 7.4 we see that the calculated value is larger than the experimental value of $28.85 \text{ J mol}^{-1} \text{ K}^{-1}$, which is very close to $7/2R$. This would be the

Table 7.4 Calculated and Experimentally Measured Values of \bar{C}_P for Several Gases at 298 K and 1 Bar

| Gas | Calculated \bar{C}_P ($\text{J mol}^{-1} \text{K}^{-1}$) | Measured \bar{C}_P ($\text{J mol}^{-1} \text{K}^{-1}$) |
|------------------|--|--|
| He | 20.79 | 20.79 |
| Ne | 20.79 | 20.79 |
| Ar | 20.79 | 20.79 |
| H ₂ | 37.41 | 28.81 |
| N ₂ | 37.41 | 29.12 |
| O ₂ | 37.41 | 29.36 |
| F ₂ | 37.41 | 31.30 |
| Cl ₂ | 37.41 | 33.91 |
| Br ₂ | 37.41 | 36.02 |
| I ₂ | 37.41 | 36.90 |
| CO ₂ | 62.37 | 37.13 |
| H ₂ O | 58.18 | 33.54 |
| SO ₂ | 58.18 | 39.82 |

value if one ignored the vibrational contribution. The absence of the vibrational contribution can be understood using quantum mechanics (Chapter 1), which predicts that the translational, rotational, and vibrational energies of a molecule are quantized. The spacing between vibrational energy levels is typically on the order of 10^{-20} J, which is larger than that between typical rotational energy levels (about 10^{-23} J), and very much larger than the typical translational energy-level spacing (about 10^{-34} J). At room temperature (298 K), $k_B T/2$ corresponds to 2.0×10^{-21} J, which is larger than the typical rotational and translational energy-level spacings, but smaller than vibrational energy-level spacings. Thus, at room temperature, energy can easily be distributed into the translational and rotational degrees of freedom, but the average amount of energy available for a single degree of freedom ($k_B T/2$) is below the minimum amount of energy required to excite most vibrational and nearly all electronic degrees of freedom. Thus, these degrees of freedom are not readily available for energy storage and so will not contribute significantly to the heat capacity. At higher temperatures, the available thermal energy, $k_B T/2$, becomes larger, and excitation of vibrational (and even electronic motion) becomes possible, leading to an increase in \bar{C}_V with increasing temperature. For example, at 3000 K, \bar{C}_P for hydrogen increases to $37.00 \text{ J mol}^{-1} \text{ K}^{-1}$, which is very close to the equipartition prediction of $37.41 \text{ J mol}^{-1} \text{ K}^{-1}$ with vibrational motion fully activated.

The preceding example of H₂ was somewhat extreme because the vibrational frequency of H₂ is very high, so at room temperature there was no contribution from vibrational modes to the heat capacity. In most other molecules, some vibrational frequencies will be low enough so that vibrational motion will contribute at least a small amount to the heat capacity at room temperature; however, this contribution will still represent only a fraction of the total vibrational contribution given in Equations 7.39 and 7.40. This is especially true in polyatomic molecules with low-frequency vibrational modes corresponding to bending motions. In some cases, it is possible to make conclusions as to the relative vibrational frequencies of two molecules simply by looking at the heat capacity. For example, the constant-pressure heat capacities

of F_2 and I_2 at 298 K are 31.30 and $36.90 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively (see Table 7.4). Both of these are linear diatomics, so translation and rotation alone account for $7/2 R = 29.10 \text{ J mol}^{-1} \text{ K}^{-1}$. Thus, the vibrational contributions to \bar{C}_P for F_2 and I_2 are 2.2 and $7.8 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. Because I_2 has a larger vibrational contribution to \bar{C}_P than F_2 , we can conclude that the vibrational frequency of I_2 is lower than that of F_2 , allowing for easier excitation of vibrational degrees of freedom given the available thermal energy. This conclusion can be verified by IR spectroscopy, which gives the vibrational frequencies for F_2 and I_2 as 919 and 214 cm^{-1} , respectively. This conclusion is interesting because we were able to make a conclusion about a molecular property of a material (vibrational frequency) solely from an examination of a macroscopic property (heat capacity).

In summary, the heat capacity is a measure of the degrees of freedom *available* for energy storage. Because quantum mechanics requires that a minimum amount of energy is needed to excite a given motion, not all degrees of freedom will be available to store energy because the energy spacing corresponding to some degrees of freedom will be larger than the available thermal energy. For gases, we should keep in mind that at room temperature, the dominant contributions to the heat capacity come from translational and rotational motion. At elevated temperatures, vibrational motion must also be taken into account. Only at very high temperatures does electronic motion play a role in determining the \bar{C}_V values.

Example 7.9

The heat capacity for CO_2 is $37.1 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298 K. What percentage of this value is due to vibrational motion? What percentage of the total possible vibrational contribution does this represent?

Strategy Use Table 7.3 to determine the $C_P = C_V + R$ for CO_2 in the absence and presence of the vibrational contribution.

Solution: CO_2 is a linear triatomic ($M = 3$) molecule. The number of possible vibrational degrees of freedom is $3M - 5 = 4$. Using Table 7.3 (or Equation 7.40), we have for translation and rotation:

$$\begin{aligned}\bar{C}_P &= \bar{C}_V + R = \left\lfloor \frac{3}{2} + 1 \right\rfloor R + R = \frac{7}{2}R \\ &= 3.5(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) = 29.1 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

For translation, rotation, and vibration:

$$\begin{aligned}\bar{C}_P &= \bar{C}_V + R = \left\lfloor \frac{3}{2} + 1 + 4 \right\rfloor R + R = 7.5R \\ &= 15(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) = 62.4 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

Ignoring electronic contributions to \bar{C}_P , which should be negligible, the vibrational contribution to the heat capacity is the difference between the experimental value and that obtained from the equipartition theorem including only translation and rotation:

$$\begin{aligned}\text{vibrational contribution to } \bar{C}_P &= 37.1 \text{ J mol}^{-1} \text{ K}^{-1} - 29.1 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 8.0 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

$$\text{fraction due to vibration} = \frac{8.0 \text{ J mol}^{-1} \text{ K}^{-1}}{37.1 \text{ J mol}^{-1} \text{ K}^{-1}} = 0.215 = 21.5\%$$

—Continued



Continued—

$$\text{total possible vibrational contribution} = 4R = 4(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) = 33.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\text{fraction of total possible vibrational contribution} = \frac{8.0 \text{ J mol}^{-1} \text{ K}^{-1}}{33.3 \text{ J mol}^{-1} \text{ K}^{-1}} = 0.240 = 24.0\%$$

So only 24.0% of the total possible vibrational contribution to the heat capacity is available at $T = 298 \text{ K}$.

Practice Exercise Use the equipartition theorem to predict the heat capacity for CIF using only rotational and translational contributions. Compare this with the experimental value of $32.1 \text{ J mol}^{-1} \text{ K}^{-1}$. What fraction of this value is due to vibrational motion?

7.4 | The Enthalpy Change for Any Reaction Can Be Calculated Using Standard Enthalpies of Formation

From Equation 7.15, we see that ΔH can be calculated if we know the actual enthalpies of all reactants and products. However, as mentioned earlier, there is no way to measure the *absolute* value of the enthalpy of a substance. Only values *relative* to an arbitrary reference can be determined. This problem is similar to the one geographers face in expressing the elevations of specific mountains or valleys. Rather than trying to devise some type of “absolute” elevation scale (perhaps based on distance from the center of Earth?), by common agreement all geographic heights and depths are expressed relative to sea level, an arbitrary reference with a defined elevation of “zero” meters or feet. Similarly, chemists have agreed on an arbitrary reference point for enthalpy.

Standard Enthalpy of Formation

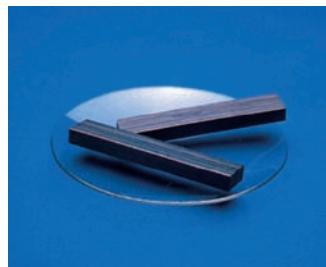
The reference point for all enthalpy expressions is called the **standard molar enthalpy of formation** (ΔH_f°) which is defined as *the heat change that results when 1 mole of a compound in its standard state is formed from its elements in their standard states*. The **standard state** of a liquid or solid substance is its most thermodynamically stable pure form at 1 bar pressure.⁶ The standard state for gases is similar, except that standard state gases are assumed to obey the ideal gas law exactly. The standard state for solutes dissolved in solution will be discussed in Chapter 10. In the notation ΔH_f° , the superscript “ $^\circ$ ” represents standard-state conditions (1 bar), and the subscript “f” stands for formation. Although the standard state does not specify a temperature, we will assume, unless otherwise stated, ΔH_f° values are measured at 25°C .

Table 7.5 lists the standard enthalpies of formation for a number of elements and compounds. (For a more complete list of ΔH_f° values, see Appendix 2.) By definition, *the standard enthalpy of formation of any element in its most stable allotropic form is zero*. Take the element oxygen as an example. Molecular oxygen (O_2) is more stable than the other allotropic form of oxygen, ozone (O_3), at 1 bar and 25°C . Thus, we can write $\Delta H_f^\circ(\text{O}_2) = 0$, but $\Delta H_f^\circ(\text{O}_3) = 142.7 \text{ kJ mol}^{-1} \neq 0$. Similarly,

6. Many texts still employ the older standard pressure of 1 atm. The change to the current standard pressure of 1 bar was recommended by the International Union of Pure and Applied Chemists (IUPAC) in 1982. Because 1 bar only differs from 1 atm by slightly more than one percent, the values of thermodynamic quantities using the two standards will generally differ by a very small amount that is often negligible.

Table 7.5 Standard Enthalpies of Formation of Some Inorganic Substances at 25°C

| Substance | $\Delta H_f^\circ \text{ kJ mol}^{-1}$ | Substance | $\Delta H_f^\circ \text{ kJ mol}^{-1}$ |
|----------------------------|--|---------------------------|--|
| $\text{Ag}(s)$ | 0 | $\text{H}_2\text{O}_2(l)$ | -187.8 |
| $\text{AgCl}(s)$ | -127.0 | $\text{Hg}(l)$ | 0 |
| $\text{Al}(s)$ | 0 | $\text{I}_2(s)$ | 0 |
| $\text{Al}_2\text{O}_3(s)$ | -1675.7 | $\text{HI}(g)$ | 25.9 |
| $\text{Br}_2(l)$ | 0 | $\text{Mg}(s)$ | 0 |
| $\text{HBr}(g)$ | -36.2 | $\text{MgO}(s)$ | -601.8 |
| C(graphite) | 0 | $\text{MgCO}_3(s)$ | -1112.9 |
| C(diamond) | 1.90 | $\text{N}_2(g)$ | 0 |
| $\text{CO}(g)$ | -110.5 | $\text{NH}_3(g)$ | -45.94 |
| $\text{CO}_2(g)$ | -393.5 | $\text{NO}(g)$ | 90.4 |
| $\text{Ca}(s)$ | 0 | $\text{NO}_2(g)$ | 33.85 |
| $\text{CaO}(s)$ | -634.9 | $\text{N}_2\text{O}_4(g)$ | 9.66 |
| $\text{CaCO}_3(s)$ | -1206.9 | $\text{N}_2\text{O}(g)$ | 81.56 |
| $\text{Cl}_2(g)$ | 0 | $\text{O}(g)$ | 249.2 |
| $\text{HCl}(g)$ | -92.3 | $\text{O}_2(g)$ | 0 |
| $\text{Cu}(s)$ | 0 | $\text{O}_3(g)$ | 142.7 |
| $\text{CuO}(s)$ | -155.2 | S(rhombic) | 0 |
| $\text{F}_2(g)$ | 0 | S(monoclinic) | 0.30 |
| $\text{HF}(g)$ | -273.3 | $\text{SO}_2(g)$ | -296.84 |
| $\text{H}(g)$ | 218.2 | $\text{SO}_3(g)$ | -395.7 |
| $\text{H}_2(g)$ | 0 | $\text{H}_2\text{S}(g)$ | -20.6 |
| $\text{H}_2\text{O}(g)$ | -241.83 | $\text{ZnO}(s)$ | -350.5 |
| $\text{H}_2\text{O}(l)$ | -285.83 | | |



graphite is a more stable allotropic form of carbon than diamond at 1 bar and 25°C, so we have ΔH_f° (C, graphite) = 0 and $\Delta \bar{H}_f^\circ$ (C, diamond) = 1.9 kJ mol⁻¹ ≠ 0.

Standard Enthalpy of Reaction

The importance of the standard enthalpies of formation is that once we know their values, we can readily calculate the **standard enthalpy of reaction** ($\Delta H_{\text{rxn}}^\circ$), defined as *the enthalpy of a reaction carried out such that all reactants and products are in their standard states*. For example, consider the hypothetical reaction



where a , b , c , and d are stoichiometric coefficients. For this reaction, $\Delta H_{\text{rxn}}^\circ$ is given by

$$\Delta H_{\text{rxn}}^\circ = [c \Delta H_f^\circ + d \Delta H_f^\circ] - [a \Delta H_f^\circ + b \Delta H_f^\circ]$$

We can generalize this equation as:

$$\Delta H_{\text{rxn}}^\circ = \sum_{\text{products}} v_p \Delta H_f^\circ(\text{products}) - \sum_{\text{reactants}} v_R \Delta H_f^\circ(\text{reactants}) \quad (7.41)$$



Graphite (top) and diamond (bottom).

where v_P and v_R denote the stoichiometric coefficients for the reactants and products, respectively, and Σ (sigma) means “the sum of.”

The advantage of Equation 7.41 is that, given a table of values for ΔH_f° for a set of compounds, we can calculate ΔH_{rxn}° for *any* possible reaction involving compounds from this set. The ΔH_f° value for a compound can be determined experimentally using either a direct method or an indirect method, depending upon the identity of the compound of interest.

The Direct Method

This method of measuring ΔH_f° works for compounds that can be readily synthesized from their elements. Suppose we want to know the enthalpy of formation of carbon dioxide. We must measure the enthalpy of the reaction when carbon (graphite) and molecular oxygen in their standard states are converted to carbon dioxide in its standard state:



We know from experience that this combustion easily goes to completion. Thus, from Equation 7.41 we can write

$$\begin{aligned}\Delta H_{rxn}^\circ &= \Delta H_f^\circ(\text{CO}_2, g) - [\Delta H_f^\circ(\text{C, graphite}) - \Delta H_f^\circ(\text{O}_2, g)] \\ &= -393.5 \text{ kJ mol}^{-1}\end{aligned}$$

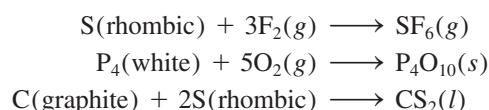
Because both graphite and O_2 are stable allotropic forms of the elements, it follows that both $\Delta H_f^\circ(\text{C, graphite})$ and $\Delta H_f^\circ(\text{O}_2, g)$ are zero. Therefore

$$\Delta H_{rxn}^\circ = \Delta \bar{H}_f^\circ(\text{CO}_2, g) = -393.5 \text{ kJ mol}^{-1}$$

or $\Delta \bar{H}_f^\circ(\text{CO}_2, g) = -393.5 \text{ kJ mol}^{-1}$

Note that arbitrarily assigning zero $\Delta \bar{H}_f^\circ$ for each element in its most stable form at the standard state does not affect our calculations in any way. Remember, in thermochemistry we are interested only in enthalpy *changes* because they can be determined experimentally whereas the absolute enthalpy values cannot. The choice of a zero “reference level” for enthalpy makes calculations easier to handle. Again referring to the terrestrial altitude analogy, we find that Mt. Everest is 2650 m higher than Mt. McKinley. This difference in altitude is unaffected by the decision to set sea level at 0 m or at 1000 m.

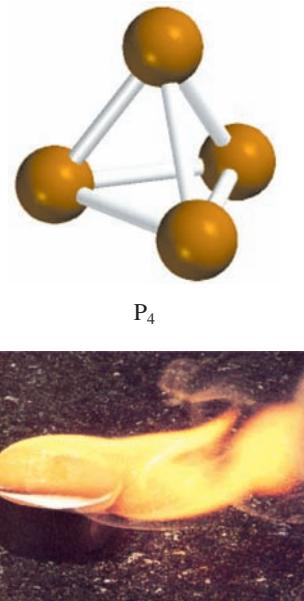
Some other compounds that can be studied by the direct method are SF_6 , P_4O_{10} , and CS_2 . The equations representing their syntheses are



Note that S(rhombic) and P(white) are the most stable allotropes of sulfur and phosphorus, respectively, at 1 bar and 25°C , so their ΔH_f° values are zero.

The Indirect Method

Many compounds cannot be directly synthesized from their elements. In some cases, the reaction proceeds too slowly, or side reactions produce substances other than the desired compound. In these cases ΔH_f° can be determined by an indirect approach, which is based on *Hess's law of summation* for extensive thermodynamic quantities,

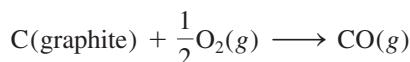


White phosphorus burns in air to form P_4O_{10} .

or simply **Hess's law**.⁷ This law can be stated as follows: *When reactants are converted to products, the change in any extensive thermodynamic state function, such as enthalpy, is the same whether the reaction takes place in one step or in a series of steps.* In other words, if we can break down the reaction of interest into a series of reactions for which $\Delta H_{\text{rxn}}^{\circ}$ can be measured, we can calculate $\Delta H_{\text{rxn}}^{\circ}$ for the overall reaction. Hess's law is based on the fact that because H is a state function, ΔH depends only on the initial and final state (that is, only on the nature of reactants and products). The enthalpy change would be the same whether the overall reaction takes place in one step or many steps.

An analogy for Hess's law is as follows. Suppose you go from the first floor to the sixth floor of a building by elevator. The gain in your gravitational potential energy (which corresponds to the enthalpy change for the overall process) is the same whether you go directly there or stop at each floor on your way up (breaking the trip into a series of steps).

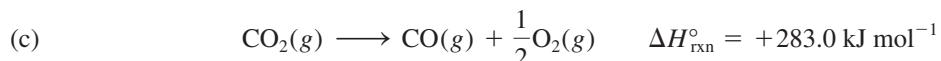
Let's say we are interested in the standard enthalpy of formation of carbon monoxide (CO). We might represent the reaction as



However, burning graphite also produces some carbon dioxide (CO_2), so we cannot measure the enthalpy change for CO directly as shown. Instead, we must employ an indirect route, based on Hess's law. It is possible to carry out the following two-step reactions, which do go to completion:

- | | | |
|-----|--|--|
| (a) | $\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$ | $\Delta H_{\text{rxn}}^{\circ} = -393.5 \text{ kJ mol}^{-1}$ |
| (b) | $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g)$ | $\Delta H_{\text{rxn}}^{\circ} = -283.0 \text{ kJ mol}^{-1}$ |

First, we reverse reaction (b) to get



Because chemical reactions can be added and subtracted just like algebraic equations, we carry out the operation (a) + (c) and obtain

- | | | |
|-------|--|--|
| (a) | $\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g)$ | $\Delta H_{\text{rxn}}^{\circ} = -393.5 \text{ kJ mol}^{-1}$ |
| (c) | $\text{CO}_2(g) \longrightarrow \text{CO}(g) + \frac{1}{2}\text{O}_2(g)$ | $\Delta H_{\text{rxn}}^{\circ} = +283.0 \text{ kJ mol}^{-1}$ |
| <hr/> | | |
| (d) | $\text{C(graphite)} + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}(g)$ | $\Delta H_{\text{rxn}}^{\circ} = -110.5 \text{ kJ mol}^{-1}$ |

Because reaction (d) represents the synthesis of 1 mole of CO from its elements, we have $\Delta H_f^{\circ}(\text{CO}) = -110.5 \text{ kJ mol}^{-1}$.

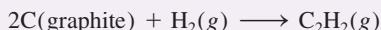
The general rule in applying Hess's law is to arrange a series of chemical equations (corresponding to a series of steps) in such a way that, when added together, all species will cancel except for the reactants and products that appear in the overall reaction. This means that we want the elements on the left and the compound of

7. Germain Henri Hess (1802–1850). Swiss chemist. Hess was born in Switzerland but spent most of his life in Russia. For formulating Hess's law, he is called the *father of thermochemistry*.

interest on the right of the arrow. Further, we often need to multiply some or all of the equations representing the individual steps by the appropriate coefficients.

Example 7.10

Calculate the standard enthalpy of formation of acetylene (C_2H_2) from its elements:



given that the standard enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are -393.5 and $-285.8\text{ kJ mol}^{-1}$, respectively, and the standard enthalpy change for the reaction



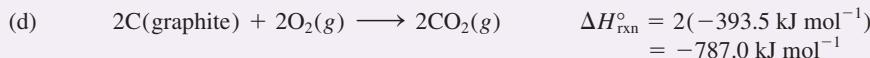
is $-2598.8\text{ kJ mol}^{-1}$.

Strategy The information given corresponds to the following set of reactions:

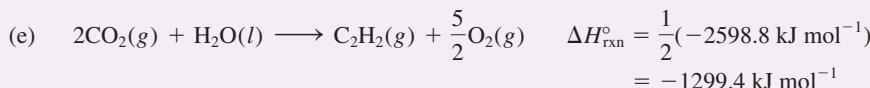
- | | |
|--|--|
| (a) $C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$ | $\Delta H_{\text{rxn}}^\circ = -393.5\text{ kJ mol}^{-1}$ |
| (b) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ | $\Delta H_{\text{rxn}}^\circ = -285.8\text{ kJ mol}^{-1}$ |
| (c) $2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l)$ | $\Delta H_{\text{rxn}}^\circ = -2598.8\text{ kJ mol}^{-1}$ |

Our goal here is to calculate the enthalpy change for the formation of C_2H_2 from its elements C and H_2 . The reaction does not occur directly, however, so we must use an indirect route using the reactions (a), (b), and (c).

Solution Looking at the synthesis of C_2H_2 , we need 2 moles of graphite as reactant. So we multiply Equation (a) by 2 to get



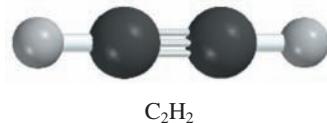
Next, we need 1 mole of H_2 as a reactant and this is provided by Equation (b). Last, we need 1 mole of C_2H_2 as a product. Equation (c) has 2 moles of C_2H_2 as a reactant so we need to reverse the equation and divide it by 2:



Adding Equations (b), (d), and (e) together, we get

- | | |
|--|--|
| (b) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ | $\Delta H_{\text{rxn}}^\circ = -285.8\text{ kJ mol}^{-1}$ |
| (d) $C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)$ | $\Delta H_{\text{rxn}}^\circ = -787.0\text{ kJ mol}^{-1}$ |
| (e) $2CO_2(g) + H_2O(l) \longrightarrow C_2H_2(g) + \frac{5}{2}O_2(g)$ | $\Delta H_{\text{rxn}}^\circ = -1299.4\text{ kJ mol}^{-1}$ |
| <hr/> | |
| $2C(\text{graphite}) + H_2(g) \longrightarrow C_2H_2(g)$ | $\Delta H_{\text{rxn}}^\circ = +226.6\text{ kJ mol}^{-1}$ |

Therefore, $\Delta H_f^\circ = \Delta H_{\text{rxn}}^\circ = 226.6\text{ kJ mol}^{-1}$. The ΔH_f° value means that when 1 mole of C_2H_2 is synthesized from 2 moles of $C(\text{graphite})$ and 1 mole of H_2 , $+226.6\text{ kJ}$ of energy in the form of heat is absorbed by the reacting system from the surroundings. Thus, this is an endothermic process.

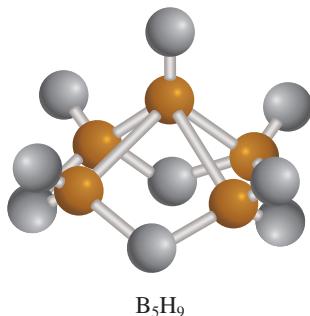


An oxyacetylene torch has a high flame temperature (3000°C) and is used to weld metals.

Continued—

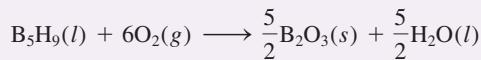
Practice Exercise Calculate the standard enthalpy of formation of carbon disulfide (CS_2) from its elements, given that the standard enthalpies of formation of $\text{CO}_2(g)$ and $\text{SO}_2(g)$ are -393.5 and $-296.4 \text{ kJ mol}^{-1}$, respectively and that the standard enthalpy of the reaction $\text{CS}_2(l) + 3\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{SO}_2(g)$ is $-1073.6 \text{ kJ mol}^{-1}$.

We can calculate the enthalpy of reactions from the values of ΔH_f° as shown in Example 7.11.



Example 7.11

Pentaborane-9 (B_5H_9) is a colorless, highly reactive liquid that will burst into flame or even explode when exposed to oxygen. The reaction is



In the 1950s, pentaborane-9 was considered as a potential rocket fuel because it produces a large amount of heat per gram. However, the solid B_2O_3 formed by the combustion of B_5H_9 is an abrasive that would quickly destroy the nozzle of the rocket, and so the idea was abandoned. Calculate the kilojoules of heat released per gram of the compound reacted with oxygen. The standard enthalpy of formation of B_5H_9 is 73.2 kJ mol^{-1} .

Strategy The enthalpy of a reaction is the difference between the sum of the enthalpies of the products and the sum of the enthalpies of the reactants each multiplied by their respective stoichiometric coefficients (Equation 7.41).

Solution Using the ΔH_f° values in Appendix 2 and Equation 7.41, we write

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \left\{ \frac{5}{2} \left[\Delta H_f^\circ(\text{B}_2\text{O}_3) + \frac{9}{2} \right] \Delta H_f^\circ[\text{H}_2\text{O}(l)] \right\} - [\Delta H_f^\circ(\text{B}_5\text{H}_9) + 6\Delta H_f^\circ(\text{O}_2)] \\ &= \left[\frac{5}{2}(-1273.5 \text{ kJ mol}^{-1}) + \frac{9}{2}(-285.8 \text{ kJ mol}^{-1}) \right] - [(73.2 \text{ kJ mol}^{-1}) + 6(0 \text{ kJ mol}^{-1})] \\ &= -4543.1 \text{ kJ mol}^{-1}\end{aligned}$$

The molar mass of B_5H_9 is 63.12 g so the energy released in the form of heat per gram is

$$\begin{aligned}\text{Heat released per gram} &= \frac{-4543.1 \text{ kJ}}{1 \text{ mol B}_5\text{H}_9} \times \frac{1 \text{ mol B}_5\text{H}_9}{63.12 \text{ g B}_5\text{H}_9} \\ &= -71.97 \text{ kJ g}^{-1}\end{aligned}$$

Check Is the negative sign consistent with the fact that B_5H_9 was considered to be used as a rocket fuel?

Practice Exercise Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. Calculate the heat released (in kJ) per gram of the compound reacted with oxygen. The standard enthalpy of formation of benzene is $49.04 \text{ kJ mol}^{-1}$.

Pentaborane-9 (B_5H_9) (see Example 7.11) is called a high-energy compound because of the large amount of energy it releases upon combustion. In general, compounds that have positive ΔH_f° values tend to release more heat as a result of combustion and to be less stable than those with negative ΔH_f° values.

7.5 | The Reaction Enthalpies Can Be Estimated from Bond Enthalpies

Recall from Section 3.2 that the bond dissociation energy, D_0 , of a particular bond in a molecule is the energy required to break that bond. For example, the bond dissociation energy of the H—H bond in H_2 is the energy required to cleave an H_2 molecule into two well-separated H atoms. In the language of the current chapter, bond dissociation energy for a diatomic molecule such as H_2 is equal to the change in energy, ΔU , for the reaction

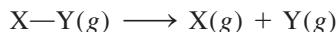


If the bond-breaking process occurs under constant-pressure conditions, however, then the energy required for bond breaking is better described by the *bond enthalpy*, rather than the bond energy. The **bond enthalpy** (ΔH_B) is *the enthalpy change, per mole of gaseous molecules, required to break a particular bond in a molecule*.

For diatomic molecules, bond enthalpies differ slightly from bond dissociation energies, and this difference can be determined using Equation 7.16 from Section 7.2:

$$\Delta H = \Delta U + RT\Delta n$$

Consider two atoms X and Y that are connected by a single bonding set of electrons to form the molecule XY. The bond energy (or enthalpy) is the energy (or enthalpy) of the reaction



For this reaction $\Delta n = 1$, so

$$\Delta H_B = D_0 + RT$$

which for $T = 298$ K gives

$$\begin{aligned}\Delta H_B(298 \text{ K}) &= D_0 + (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \\ &= D_0 + 2.48 \text{ kJ mol}^{-1}\end{aligned}$$

Thus, the bond enthalpy of a diatomic molecule can be determined from the bond dissociation energy (such as those listed in Table 3.3) at 298 K by adding 2.48 kJ mol^{-1} .

For example, the bond dissociation energy for H_2 is 432.9 kJ mol^{-1} , so the bond enthalpy for H_2 is $(432.9 + 2.48) \text{ kJ mol}^{-1} = 436.4 \text{ kJ mol}^{-1}$. This conversion is useful because experiments on gases typically measure the bond enthalpy, but theoretical calculations often determine the bond dissociation energy directly. For polyatomic molecules, the enthalpy required to break a particular bond type (say C—H or C=O) will vary among the many compounds that contain these bond types. For this reason, bond enthalpies for polyatomic molecules are reported as *average bond* enthalpies. For example, we can measure the energy of the O—H bond in 10 different polyatomic molecules and obtain the average O—H bond energy by dividing the sum of the bond energies by 10. Table 7.6 lists the exact or average bond enthalpies of a number of diatomic and polyatomic molecules. Although bond energies and bond enthalpies are generally quite similar in magnitude (at least for diatomic molecules), the difference can be important in very accurate work.

Nearly all chemical reactions involve the breaking and/or formation of bonds. Therefore, knowing the bond enthalpies and hence the stability of molecules reveals something about the thermochemical nature of the reactions that molecules undergo. In many cases, it is possible to predict the approximate enthalpy of reaction by using

Table 7.6 Some Bond Enthalpies of Diatomic Molecules and Average Bond Energies for Bonds in Polyatomic Molecules*

| Bond | Bond Enthalpy (kJ mol ⁻¹) | Bond | Bond Enthalpy (kJ mol ⁻¹) |
|------------------|--|-------|--|
| H—H | 436.4 | N—N | 193 |
| H—N | 393 | N=N | 418 |
| H—O | 460 | N≡N | 941.4 |
| H—S | 368 | N—O | 176 |
| H—P | 326 | N—P | 209 |
| H—F | 568.2 | O—O | 142 |
| H—Cl | 431.9 | O=O | 498.7 |
| H—Br | 366.1 | O—P | 502 |
| H—I | 298.3 | O=S | 469 |
| C—H | 414 | P—P | 197 |
| C—C | 347 | P=P | 489 |
| C=C | 620 | S—S | 268 |
| C≡C | 812 | S=S | 352 |
| C—N | 276 | F—F | 156.9 |
| C=N | 615 | Cl—Cl | 242.7 |
| C≡N | 891 | Br—Br | 192.5 |
| C—O | 351 | I—I | 151.0 |
| C=O [†] | 745 | C—F | 484 |
| C—P | 263 | C—Cl | 338 |
| C—S | 255 | C—Br | 276 |
| C=S | 477 | C—I | 238 |

*Bond enthalpies for diatomic molecules (in red) have more significant figures than for bonds in polyatomic molecules because the bond energies of diatomic molecules are directly measurable quantities and not averaged over many compounds.

[†]The C=O bond enthalpy in CO₂ is 799 kJ mol⁻¹.

bond enthalpy data, such as that listed in Table 7.6. Because energy is always required to break chemical bonds and chemical bond formation is always accompanied by the release of energy, we can estimate the enthalpy of a reaction by counting the total number and kind of bonds broken and formed in the reaction and recording the corresponding energy changes. The enthalpy of reaction in the *gas phase* is given by

$$\Delta H_{rxn}^{\circ} = \sum_{\substack{\text{bonds} \\ \text{broken}}} \Delta H_B - \sum_{\substack{\text{bonds} \\ \text{formed}}} \Delta H_B = \text{total energy input} - \text{total energy released} \quad (7.42)$$

Equation 7.42 is consistent with the usual sign convention for ΔH_{rxn}° . Thus, if the total energy input exceeds the total energy released, ΔH_{rxn}° is positive and the reaction is endothermic [Figure 7.14(a)]. On the other hand, if more energy is released than is absorbed, ΔH_{rxn}° is negative and the reaction is exothermic [Figure 7.14(b)]. If the reactants and products are all diatomic molecules, then Equation 7.42 will yield accurate results because the bond enthalpies of diatomic molecules are accurately known. However, if some or all of the reactants and products are polyatomic

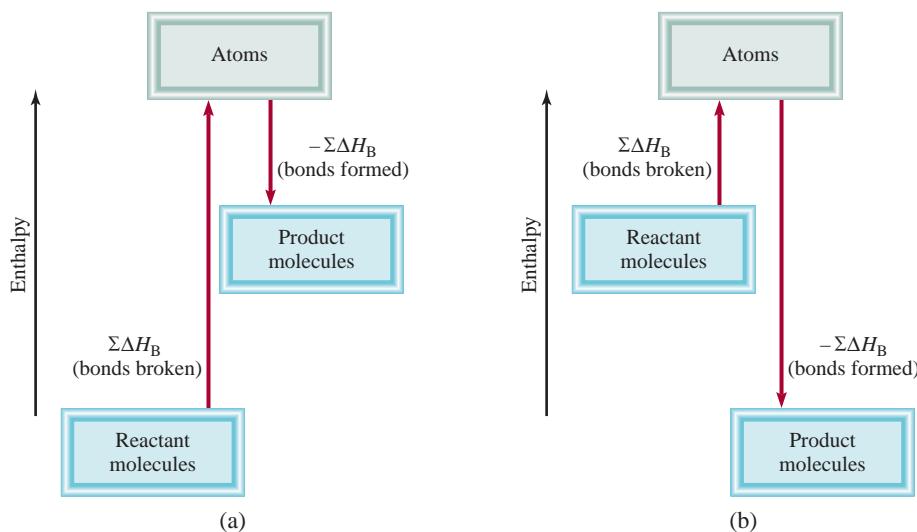


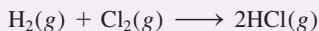
Figure 7.14 Bond enthalpy changes in (a) an endothermic reaction and (b) an exothermic reaction.

molecules, Equation 7.42 will yield only approximate results because the bond enthalpies used will be average values.

For diatomic molecules, Equation 7.42 is equivalent to Equation 7.41, so the results obtained from these two equations should correspond, as Example 7.12 illustrates.

Example 7.12

- (a) Use Equation 7.42 to calculate the enthalpy of reaction for the process



- (b) Compare your result with that obtained using standard enthalpies of formation (Equation 7.41).

Strategy Bond breaking is an energy-absorbing (endothermic) process, and bond making is an energy-releasing (exothermic) process. Therefore, the overall energy change is the difference between these two opposing processes, as described by Equation 7.42.

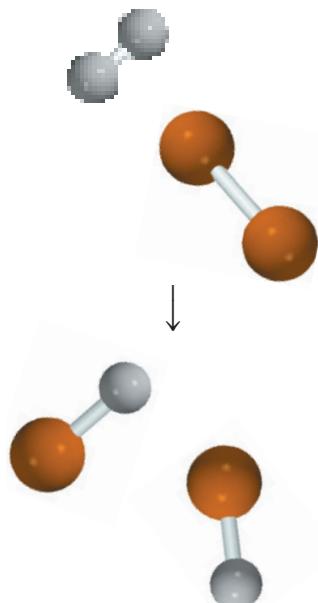
Solution (a) We start by counting the number of bonds broken and the number of bonds formed and the corresponding energy changes. This is best done by creating a table:

| Type of Bonds Broken | Number of Bonds Broken | Bond Enthalpy (kJ mol^{-1}) | Enthalpy Change (kJ mol^{-1}) |
|----------------------|------------------------|--|--|
| H—H | 1 | 436.4 | 436.4 |
| Cl—Cl | 1 | 242.7 | 242.7 |
| Type of Bonds Formed | Number of Bonds Formed | Bond Enthalpy (kJ mol^{-1}) | Enthalpy Change (kJ mol^{-1}) |
| H—Cl | 2 | 431.9 | 863.8 |

Next, we obtain the total enthalpy input and total enthalpy released:

$$\text{total enthalpy input} = \sum_{\substack{\text{bonds} \\ \text{broken}}} \Delta H_B = 436.4 \text{ kJ mol}^{-1} + 242.7 \text{ kJ mol}^{-1} = 679.1 \text{ kJ mol}^{-1}$$

$$\text{total enthalpy released} = \sum_{\substack{\text{bonds} \\ \text{formed}}} \Delta H_B = 2(431.9 \text{ kJ mol}^{-1}) = 863.8 \text{ kJ mol}^{-1}$$



—Continued

Continued—

Using Equation 7.42, we write

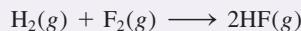
$$\Delta H_{\text{rxn}}^{\circ} = \sum_{\text{bonds broken}} \Delta H_B - \sum_{\text{bonds formed}} \Delta H_B = 679.1 \text{ kJ mol}^{-1} - 863.8 \text{ kJ mol}^{-1} = -184.7 \text{ kJ mol}^{-1}$$

- (b) Alternatively, we can use Equation 7.41 and the data in Appendix 2 to calculate the enthalpy of reaction:

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= 2\bar{\Delta H}_f^{\circ}(\text{HCl}) - [\bar{\Delta H}_f^{\circ}(\text{H}_2) + \bar{\Delta H}_f^{\circ}(\text{Cl}_2)] \\ &= (2)(-92.3 \text{ kJ mol}^{-1}) - [0 + 0] \\ &= -184.6 \text{ kJ mol}^{-1}\end{aligned}$$

Check Because the reactants and products are all diatomic molecules, we expect the results of Equations 7.42 and 7.41 to be the same. The small discrepancy here is due to different ways of rounding off.

Practice Exercise Calculate the enthalpy of the reaction

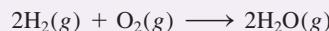


using (a) Equation 7.42 and (b) Equation 7.41.

Example 7.13 uses Equation 7.42 to estimate the enthalpy of a reaction involving a polyatomic molecule.

Example 7.13

Estimate the enthalpy change for the combustion of hydrogen gas:



Strategy We follow the same procedure as was used in Example 7.10. Note, however, that H_2O is a polyatomic molecule, so we need to use the average bond energy value for the O—H bond.

Solution Construct the following table:

| Type of Bonds Broken | Number of Bonds Broken | Bond Enthalpy (kJ mol^{-1}) | Enthalpy Change (kJ mol^{-1}) |
|----------------------|------------------------|--|--|
| H—H | 2 | 436.4 | 872.8 |
| O=O | 1 | 498.7 | 498.7 |
| Type of Bonds Formed | Number of Bonds Formed | Bond Enthalpy (kJ mol^{-1}) | Enthalpy Change (kJ mol^{-1}) |
| O—H | 4 | 460 | 1840 |

Next, obtain the total enthalpy input and total enthalpy released:

$$\text{total enthalpy input} = \sum_{\text{bonds broken}} \Delta H_B = 872.8 \text{ kJ mol}^{-1} + 498.7 \text{ kJ mol}^{-1} = 1371.5 \text{ kJ mol}^{-1}$$

$$\text{total enthalpy released} = \sum_{\text{bonds formed}} \Delta H_B = 1840 \text{ kJ mol}^{-1}$$

—Continued

Continued—

Using Equation 7.42, we write

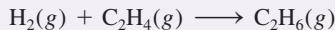
$$\Delta H_{\text{rxn}}^{\circ} = \sum_{\text{bonds broken}} \Delta H_B - \sum_{\text{bonds formed}} \Delta H_B = 1371.5 \text{ kJ mol}^{-1} - 1840 \text{ kJ mol}^{-1} = -469 \text{ kJ mol}^{-1}$$

This result is only an estimate because the bond enthalpy of an O—H bond is an average quantity. Alternatively, we can use Equation 7.40 and the data in Appendix 2 to calculate the enthalpy of reaction:

$$\begin{aligned}\Delta H_{\text{rxn}}^{\circ} &= 2\bar{\Delta H_f^{\circ}}[\text{H}_2\text{O}(g)] - \{2\Delta H_f^{\circ}[\text{H}_2(g)] + \Delta H_f^{\circ}[\text{O}_2(g)]\} \\ &= 2(-241.8 \text{ kJ mol}^{-1}) - [0 + 0] \\ &= -483.6 \text{ kJ mol}^{-1}\end{aligned}$$

Check The estimated value based on average bond enthalpies is close, but not exactly equal, to the value calculated using ΔH_f° data. In general, Equation 7.42 works best for reactions that are either quite endothermic or quite exothermic, that is, reactions for which $\Delta H_{\text{rxn}}^{\circ} > 100 \text{ kJ mol}^{-1}$ or for which $\Delta H_{\text{rxn}}^{\circ} < -100 \text{ kJ mol}^{-1}$.

Practice Exercise For the reaction



- Use the bond energy values in Table 7.6 to estimate the enthalpy of reaction.
- Use standard enthalpies of formation to calculate the enthalpy of reaction. (ΔH_f° values for H_2 , C_2H_4 , and C_2H_6 are 0, 52.3, and $-84.7 \text{ kJ mol}^{-1}$, respectively.)

7.6 | Enthalpy Changes Also Accompany Physical Transformations

Although we have focused so far primarily on the thermal energy effects resulting from chemical reactions, many physical processes also involve the absorption or release of heat. Examples include phase transformations, such as the melting of ice or the condensation of water vapor. Enthalpy changes occur as well when a solute dissolves in a solvent or when a solution is diluted.

Enthalpy Changes in Phase Transitions

Phase transitions generally involve changes in the density and/or structural rearrangement of the molecules in a system. Because such changes alter the spatial arrangement of the molecules relative to one another, and thus the intermolecular interactions, phase transitions are generally accompanied by the evolution or absorption of energy in the form of heat. Because phase transitions take place at constant pressure, this heat energy is equal to the change in enthalpy for the transition process of interest. In Chapter 5, we discussed three common types of phase transformations: vaporization, fusion, and sublimation. Here we discuss the magnitude of enthalpy changes for these transformations, paying particular attention to the role played by intermolecular forces.

Enthalpy of Vaporization

Vaporization is the process by which a liquid transforms into a vapor (gas). The **molar enthalpy (or heat) of vaporization** (ΔH_{vap}) is *the energy required to vaporize 1 mole*

Table 7.7 Molar Enthalpies of Vaporization for Selected Substances at Their Normal Boiling Points

| Substance | Boiling Point* (°C) | ΔH_{vap} (kJ mol ⁻¹) |
|---|---------------------|---|
| Argon (Ar) | −186 | 6.3 |
| Benzene (C ₆ H ₆) | 80.1 | 31.0 |
| Ethanol (C ₂ H ₅ OH) | 78.3 | 39.3 |
| Diethyl ether (C ₂ H ₅ OC ₂ H ₅) | 34.6 | 26.0 |
| Mercury (Hg) | 357 | 59.0 |
| Methane (CH ₄) | −164 | 9.2 |
| Water (H ₂ O) | 100 | 40.79 |

*Measured at 1 atm.

of liquid.⁸ The molar heat of vaporization is directly related to the strength of the intermolecular forces that exist in a liquid. If the intermolecular attractions are strong, the energy required to free the molecules from the liquid phase is large. Such a liquid has a high molar enthalpy of vaporization and a low vapor pressure (see Section 6.1).

A practical way to demonstrate the molar heat of vaporization is to rub an alcohol such as ethanol (C₂H₅OH) or isopropanol (C₃H₇OH) on your hands. These alcohols have a lower $\Delta H_{\text{vap}}^{\circ}$ than water, so the heat from your hands is enough to increase the kinetic energy of the alcohol molecules and evaporate them. As a result of the loss of heat, your hands feel cool. This process is similar to perspiration, which is one of the means by which the human body maintains a constant temperature. Because of the strong intermolecular hydrogen bonding that exists in water, a considerable amount of energy is needed to vaporize the water in perspiration from the surface of the skin. This energy is supplied by the heat generated in various metabolic processes.

Table 7.7 lists ΔH_{vap} values for a number of liquids at their normal boiling points (at 1 atm). These data show that substances with high boiling points tend to have large enthalpies of vaporization. To understand this trend, you must recognize that both the boiling point and the heat of vaporization are measures of intermolecular attraction in the liquid. For example, argon (Ar) and methane (CH₄), which have weak dispersion forces, have low boiling points and small molar enthalpies of vaporization. Diethyl ether (C₂H₅OC₂H₅) has a dipole moment, and the dipole-dipole forces account for its moderately high boiling point and ΔH_{vap} . Both ethanol (C₂H₅OH) and water have strong hydrogen bonding, which accounts for their high boiling points and large ΔH_{vap} values. Strong metallic bonding causes mercury to have the highest boiling point and ΔH_{vap} of this group of liquids. Interestingly, the boiling point of benzene, which is nonpolar, is comparable to that of ethanol. Benzene has a high polarizability due to the distribution of its electrons in the delocalized π molecular orbitals, and the dispersion forces among benzene molecules can be as strong as or even stronger than dipole-dipole forces and/or hydrogen bonds.

8. The enthalpy change in any phase transition is sometimes referred to as the *latent heat* of that transition. For example, ΔH_{vap} is often called the *latent heat of vaporization*.

Table 7.8**Molar Enthalpies of Fusion for Select Substances at Their Normal Melting Points**

| Substance | Melting Point* (°C) | ΔH_{fus} (kJ mol ⁻¹) |
|---|---------------------|---|
| Argon (Ar) | -190 | 1.3 |
| Benzene (C ₆ H ₆) | 5.5 | 10.9 |
| Ethanol (C ₂ H ₅ OH) | -117.3 | 7.61 |
| Diethyl ether (C ₂ H ₅ OC ₂ H ₅) | -116.2 | 6.90 |
| Mercury (Hg) | -39 | 23.4 |
| Methane (CH ₄) | -183 | 0.84 |
| Water (H ₂ O) | 0 | 6.01 |

*Measured at 1 atm.

Enthalpy of Fusion

The **molar enthalpy (or heat) of fusion** (ΔH_{fus}) is the energy required to melt 1 mole of solid. Table 7.8 lists the molar enthalpies of fusion at the melting points (ΔH_{fus}) for the substances in Table 7.7. Notice that ΔH_{fus} is smaller than ΔH_{vap} for each substance. This occurs because considerably more energy is needed to overcome the attractive forces between liquid molecules to completely separate them into vapor molecules than is needed to rearrange solid molecules into liquid molecules.

Based on Table 7.8, there is also a rough correlation between melting temperature and the enthalpy of fusion. Weakly interacting substances, such as argon and methane, generally have lower melting points and enthalpies of fusion than substances with stronger intermolecular attractions, such as benzene and water. However, the correlation between the melting temperature and ΔH_{fus} is not as strong as that between the boiling temperature and ΔH_{fus} . For example, mercury melts at -39°C, but has a much larger enthalpy of fusion than benzene (23.4 kJ mol⁻¹ vs. 10.9 kJ mol⁻¹) despite the fact that benzene has the higher melting point (5.5°C). During fusion, the molecules are simply rearranged and not completely pulled apart, so the enthalpy change will depend upon factors other than the strength of intermolecular forces, such as crystal structure and liquid density.

Enthalpy of Sublimation

Sublimation is the direct conversion of a solid to a vapor, so the **molar enthalpy of sublimation** (ΔH_{sub}) is the energy required to sublime 1 mole of a solid. In general, the molecules in a solid are more tightly held together by intermolecular forces than those in a liquid, so ΔH_{sub} is larger than ΔH_{vap} . If ΔH_{sub} , ΔH_{vap} , and ΔH_{fus} could all be measured at the same temperature (such as is possible at the triple point of water), we would have

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}} \quad (7.43)$$

Equation 7.43 is an application of Hess's law (Section 7.5), because the enthalpy change for the overall process is the same whether the substance changes directly from the solid to the vapor (sublimation) or from the solid to the liquid and then to the vapor (fusion + vaporization). If the enthalpies for the three processes (sublimation, fusion, and vaporization) are measured at different temperatures, which they often are, then Equation 7.43 can only be used as an approximation.

Heating Curves

When a liquid or solid is far from a phase transition temperature, any addition of energy in the form of heat at constant pressure (q_p) leads to an increase in the temperature (ΔT) of the system, as shown by rearranging Equation 7.18:

$$\Delta T = \frac{q_p}{C_p} \quad (7.44)$$

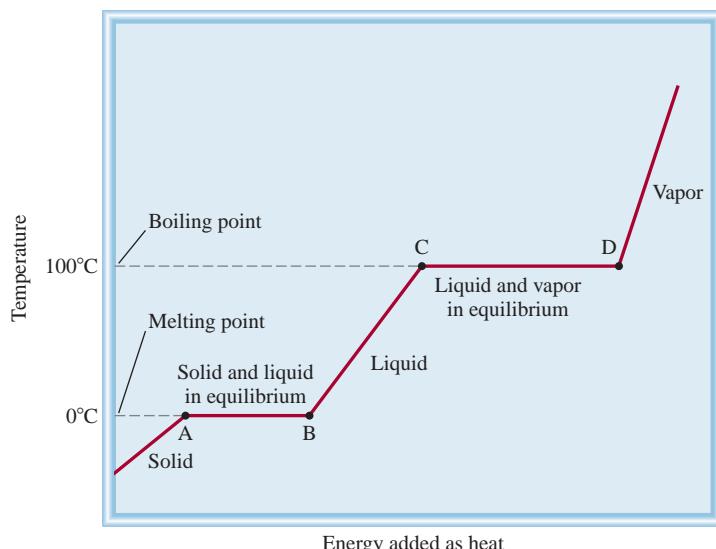
where C_p is the constant-pressure heat capacity of the solid or liquid. When the substance reaches a transition temperature, however, energy added as heat to the system does not raise the temperature. Instead, it supplies the energy necessary to change the phase of the material. The amount of heat energy required to convert n moles of substance from one phase to another is given by

$$q_p = n \Delta H_{\text{trans}} \quad (7.45)$$

where ΔH_{trans} is the molar enthalpy of the transition. Consider, for example, the heating of a block of ice, originally at -30°C , to a final temperature of 130°C , where the heating is done at a constant pressure of 1 atm. Figure 7.15 shows the *heating curve* for this process, which is a plot of the temperature as a function of the amount of heat added.

Initially, the addition of heat raises the temperature of the ice. The slope of the heating curve is the reciprocal of the heat capacity of ice (Equation 7.44). When the temperature reaches the melting point of ice (0°C), further addition of heat goes entirely into converting the ice into water according to Equation 7.45, using ΔH_{fus} for the enthalpy of transition. During this conversion, the temperature remains constant. After the ice is completely transformed to liquid water, the temperature will begin to rise again upon the further addition of heat according to Equation 7.44, except now the slope is determined by the reciprocal of the heat capacity of liquid water. Because the heat capacity of liquid water ($\bar{C}_p = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}$) is greater than that of ice ($\bar{C}_p = 38.0 \text{ J mol}^{-1} \text{ K}^{-1}$), the slope of the heating curve is less in the region between 0°C and 100°C than in the region from -30°C to zero. The heating

Figure 7.15 The heating curve (temperature versus energy added as heat) for the heating of water from -30°C to a final temperature of 130°C . Because $\Delta\bar{H}_{\text{fus}}^\circ$ is less than $\Delta\bar{H}_{\text{vap}}^\circ$, less heat is required to melt the ice at 0°C than to boil the liquid water at 100°C . This explains why AB is shorter than CD. The steepness of the solid, liquid, and vapor heating lines is determined by the heat capacity of water in each state.



of the liquid continues until the temperature reaches the boiling point of water (100°C) at which point the temperature remains constant as the liquid is converted to vapor. Following complete vaporization, the temperature rises again with a slope that is greater than that for heating ice or water because the constant pressure molar heat capacity of water vapor is $33.6 \text{ J mol}^{-1} \text{ K}^{-1}$, which is smaller than that for both liquid water and ice.

Example 7.14 shows how to calculate the total energy required to heat a system through a phase change at constant pressure.

Example 7.14

Calculate the amount of energy (in kJ) needed to heat 346 g of liquid water from 0°C to 182°C . Assume that the specific heat capacity of water is $4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ over the entire liquid range and that the specific heat of steam is $1.99 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$.

Strategy The process consists of three steps, heating water from 0°C to 100°C , evaporating water at 100°C , and heating steam from 100°C to 182°C . The heat change (q) at each stage is given by $q = m C_s \Delta T$ (Equation 7.19), where m is the mass of water, C_s is the specific heat, and ΔT is the temperature change. At the phase change (vaporization), q is given by $n \Delta H_{\text{vap}}$, where n is the number of moles of water.

Solution The calculation can be broken down into three steps:

Step 1: Heating water from 0°C to 100°C

Using Equation 7.20, we write

$$\begin{aligned} q_1 &= mC_s\Delta T \\ &= (346 \text{ g})(4.184 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1})(100^{\circ}\text{C} - 0^{\circ}\text{C}) = 1.45 \times 10^5 \text{ J} = 145 \text{ kJ} \end{aligned}$$

Step 2: Evaporating 346 g of water at 100°C (a phase change)

According to Table 7.7, $\Delta H_{\text{vap}} = 40.79 \text{ kJ mol}^{-1}$ for water, so

$$\begin{aligned} q_2 &= n\Delta H_{\text{vap}} \\ &= \left(\frac{346 \text{ g}}{18.02 \text{ g mol}^{-1}} \right)(40.79 \text{ kJ mol}^{-1}) = 783 \text{ kJ} \end{aligned}$$

Step 3: Heating steam from 100°C to 182°C

$$\begin{aligned} q_3 &= mC_s\Delta T \\ &= (346 \text{ g})(1.99 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1})(182^{\circ}\text{C} - 100^{\circ}\text{C}) = 5.65 \times 10^4 \text{ J} = 56.5 \text{ kJ} \end{aligned}$$

The overall energy required is given by

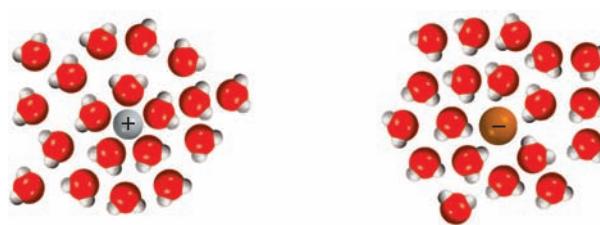
$$\begin{aligned} q_{\text{overall}} &= q_1 + q_2 + q_3 \\ &= 145 \text{ kJ} + 783 \text{ kJ} + 56.5 \text{ kJ} = 985 \text{ kJ} \end{aligned}$$

Note that the dominant contribution to this heating process comes from the vaporization step.

Check All three qs have a positive sign, because heat is absorbed at all three stages to raise the temperature from 0°C to 182°C .

Practice Exercise Calculate the heat released when 68.0 g of steam at 124°C is condensed to water at 45°C .

Figure 7.16 Hydration of Na^+ and Cl^- ions. Note that the arrangement of the water molecules surrounding the ion are considerably different for these two ions. Around the Na^+ ions, the surrounding water molecules orient so that their negatively charged ends (the oxygen atoms) are adjacent to the cation. Around Cl^- , the positively charged end of the water molecules (the hydrogen atom) is adjacent to the anion.



Enthalpy of Solution and Dilution

In addition to the enthalpies of phase transitions just discussed, enthalpy changes also occur when two substances are mixed, such as when a solute is dissolved in a solvent (the enthalpy of solution) or when a solution is diluted (the enthalpy of dilution).

Enthalpy of Solution

In the vast majority of cases, dissolving a solute in a solvent produces measurable heat change. At constant pressure, the heat change is equal to the enthalpy change. The **enthalpy (or heat) of solution** (ΔH_{soln}) is the *heat absorbed when a certain amount of solute dissolves in a certain amount of solvent*. When this quantity is measured at standard pressure (1 bar), it is called the *standard enthalpy of solution* ($\Delta H_{\text{soln}}^\circ$).

The quantity ΔH_{soln} represents the difference between the enthalpy of the final solution and the enthalpies of its original components (that is, the solute and solvent) before they are mixed. Thus,

$$\Delta H_{\text{soln}} = H_{\text{soln}} - H_{\text{components}} \quad (7.46)$$

Neither H_{soln} nor $H_{\text{components}}$ can be measured, but their difference (ΔH_{soln}) can be readily determined using calorimetry. Like other enthalpy changes, ΔH_{soln} is positive for endothermic (heat-absorbing) processes and negative for exothermic (heat-generating) processes.

To better understand the heat of solution, consider what happens when solid NaCl (an ionic compound) dissolves in water. In solid NaCl, the Na^+ and Cl^- ions are held together by strong positive-negative (electrostatic) forces, but when a small crystal of NaCl dissolves in water, the three-dimensional network of ions breaks into its individual units. (The structure of solid NaCl is shown in Figure 0.12.) The separated Na^+ and Cl^- ions are stabilized in solution by their interaction with water molecules, which completely surround the ions (Figure 7.16).

These ions are said to be *hydrated*. Water molecules shield the Na^+ and Cl^- ions from each other and effectively reduce the electrostatic attraction that held them together in the solid state. Thus, the water molecules act like a good electrical insulator. The heat of solution is defined by the following process:



Dissolving an ionic compound such as NaCl in water involves complex interactions among the solute and solvent species. For the sake of analysis, however, we can imagine that the solution process takes place in the two separate steps illustrated in Figure 7.17.

First, the Na^+ and Cl^- ions in the solid crystal are separated from each other and converted to the gaseous state:



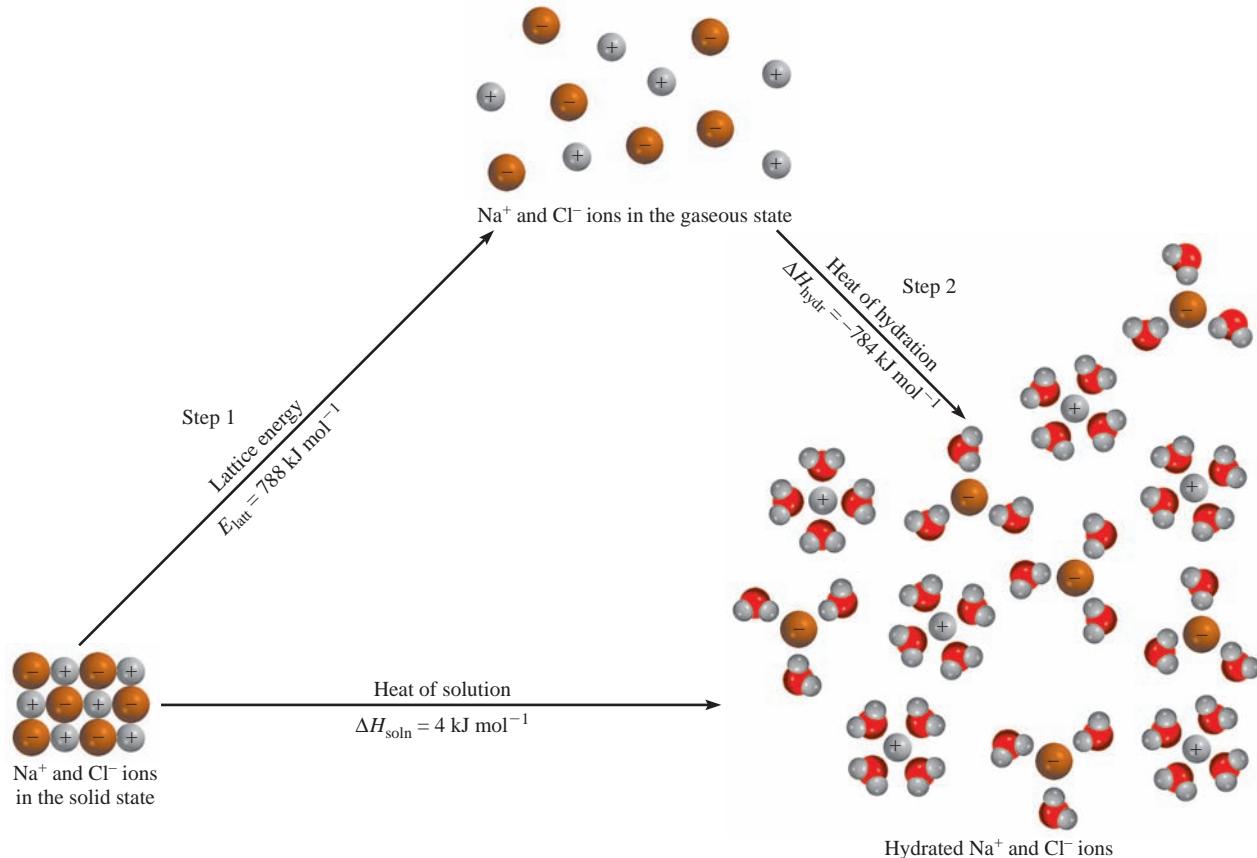
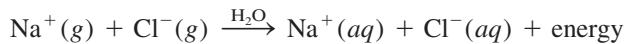
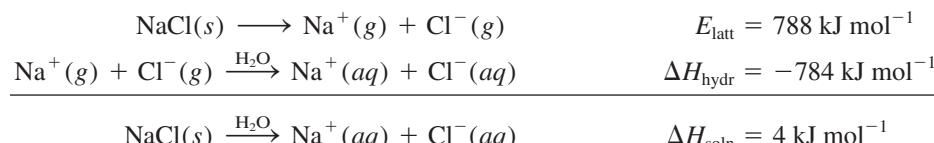


Figure 7.17 The solution process for NaCl. The process can be considered to occur in two separate steps: (1) separation of ions from the crystal state to the gaseous state and (2) hydration of the gaseous ions. The heat of solution is equal to the energy changes for these two steps, $\Delta H_{\text{soln}} = E_{\text{latt}} + \Delta H_{\text{hydr}}$.

The energy required to completely separate 1 mole of a solid ionic compound into gaseous ions is called the **lattice energy** (E_{latt}). The lattice energy of NaCl is 788 kJ mol⁻¹. In other words, we need 788 kJ of energy to break 1 mole of solid NaCl into 1 mole of Na⁺ ions and 1 mole of Cl⁻ ions. Next, the “gaseous” Na⁺ and Cl⁻ ions enter the water and become hydrated:



The enthalpy change associated with hydration is called the **enthalpy** (or heat) of **hydration** (ΔH_{hydr}). The heat of hydration is a negative quantity for cations and anions. Applying Hess's law, it is possible to treat ΔH_{soln} as the sum of two related quantities, the lattice energy (E_{latt}) and the heat of hydration ΔH_{hydr} :



Therefore, when 1 mole of NaCl dissolves in water, 4 kJ of heat is absorbed from the surroundings (the beaker containing the solution becomes slightly colder). The ΔH_{soln}

Table 7.9
**Infinite Dilution
Enthalpies of Solution for Some Ionic Compounds**

| Compound | ΔH_{soln} (kJ mol ⁻¹) |
|---------------------------------|---|
| LiCl | -37.1 |
| CaCl ₂ | -82.8 |
| NaCl | 4.0 |
| KCl | 17.2 |
| NH ₄ Cl | 15.2 |
| NH ₄ NO ₃ | 26.2 |

of 4 kJ mol⁻¹ calculated for NaCl is valid if the solution formed is dilute. When NaCl is added to a concentrated solution the enthalpy change will differ due to interactions of the Na⁺ and Cl⁻ ions already in the solution. For this reason, the ΔH_{soln} just calculated is often referred to as the *infinite dilution* (or *limiting enthalpy of solution*). Table 7.9 lists the infinite dilution enthalpies of solution of several ionic compounds in water. Depending on the nature of the cation and anion involved, ΔH_{soln} for an ionic compound may be either negative (exothermic) or positive (endothermic).

The enthalpy of solution for ammonium nitrate (NH₄NO₃) is very positive (highly endothermic) and much larger than the other values in Table 7.9. As a result, the dissolution of NH₄NO₃ is used in many commercial disposable cold packs. These cold packs contain two separate chambers, one containing solid NH₄NO₃ and one containing water. When the seal between the two chambers is broken, the ammonium nitrate dissolves in the water. This endothermic process absorbs a great deal of heat energy, leading to a significant drop in the temperature of the pack. (For an example of the use of exothermic reactions in the construction of hot packs, see Problem 7.69.)

Heat of Dilution

When a solution is *diluted*—that is, when more solvent is added to lower the overall concentration of the solute—additional heat is usually given off or absorbed. The *enthalpy* (or *heat*) of dilution (ΔH_{dil}) is the *heat change associated with the dilution process*. If a certain solution process is endothermic and the solution is subsequently diluted, *more* heat will be absorbed by the same solution from the surroundings. In an exothermic solution process, more heat will be liberated if additional solvent is added to dilute the solution. Therefore, always be cautious when diluting a solution in the laboratory.

Because of its highly exothermic heat of dilution, concentrated sulfuric acid (H₂SO₄) can be particularly hazardous if it must be diluted with water. Concentrated H₂SO₄ consists of 98 percent acid and 2 percent H₂O by mass. Diluting it with water releases so much heat to the surroundings (the process is so exothermic) that you must *never* attempt to dilute the concentrated acid by adding water to it. The heat generated could cause the acid solution to boil and splatter. The recommended procedure is to add the concentrated acid slowly to the water (while constantly stirring).

7.7 | The Temperature Dependence of Reaction Enthalpies Can Be Determined from Heat Capacity Data

So far all our calculations for $\Delta H_{\text{rxn}}^{\circ}$ have been for room temperature (298 K). Suppose, however, that our reaction of interest takes place at 400 K. How would we determine the heat energy absorbed or released by the reaction at this temperature? If high precision is not required, it is often sufficient to assume that $\Delta H_{\text{rxn}}^{\circ}$ is approximately independent of temperature and to use the value of $\Delta H_{\text{rxn}}^{\circ}$ (298 K) for $\Delta H_{\text{rxn}}^{\circ}$ (350 K). For high-precision calculations, however, the change in $\Delta H_{\text{rxn}}^{\circ}$ as we go from $T_1 = 298$ K to our temperature of interest (T_2) might be significant. One way to find the value at T_2 would be to repeat the measurement of $\Delta H_{\text{rxn}}^{\circ}$ directly at T_2 or to find a table of ΔH_f° values measured at T_2 , but doing experiments is time consuming and finding an appropriate table of data at exactly the temperature we want is rarely possible. Fortunately, using thermodynamics, it is possible to obtain $\Delta H_{\text{rxn}}^{\circ}$ values at T_2 from data tabulated at another temperature, T_1 , without having to do another experiment.

For any reaction, the standard enthalpy change at a particular temperature is

$$\Delta H_{\text{rxn}}^{\circ} = \sum_{\text{products}} H^{\circ} - \sum_{\text{reactants}} H^{\circ} \quad (7.47)$$

To see how the standard enthalpy of reaction ($\Delta H_{\text{rxn}}^\circ$) changes with temperature, recall that $dH = C_P dT$ (Equation 7.26) at constant pressure. Thus,

$$\begin{aligned} H^\circ(T_2) &= H^\circ(T_1) + \int_{T_1}^{T_2} C_P dT \\ &\approx H^\circ(T_1) + C_P(T_2 - T_1) = H^\circ(T_1) + C_P \Delta T \end{aligned} \quad (7.48)$$

if C_P can be treated as constant over the temperature range of interest. Combining Equations 7.47 and 7.48 gives

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ(T_2) &= \sum_{\text{products}} \left[H^\circ(T_1) + C_P \Delta T \right] - \sum_{\text{reactants}} \left[H^\circ(T_1) + C_P \Delta T \right] \\ &= \left[\sum_{\text{products}} H^\circ(T_1) - \sum_{\text{reactants}} H^\circ(T_1) \right] - \left[\sum_{\text{products}} C_P^\circ - \sum_{\text{reactants}} C_P^\circ \right] \Delta T \\ &= \Delta H_{\text{rxn}}^\circ(T_1) + \left(\sum_{\text{products}} C_P^\circ - \sum_{\text{reactants}} C_P^\circ \right) \Delta T \end{aligned}$$

or

$$\Delta H_{\text{rxn}}^\circ(T_2) = \Delta H_{\text{rxn}}^\circ(T_1) + \Delta C_{P,\text{rxn}}^\circ \Delta T \quad (7.49)$$

where we have defined the standard reaction heat capacity as

$$\Delta C_{P,\text{rxn}}^\circ = \sum_{\text{products}} v_p \bar{C}_P^\circ - \sum_{\text{reactants}} v_R \bar{C}_P^\circ \quad (7.50)$$

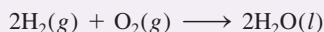
and where v_p and v_R are the stoichiometric coefficients for the products and reactants, respectively, and \bar{C}_P° is the standard molar heat capacity.

Equation 7.49 is known as **Kirchhoff's law**, after the German physicist Gustav-Robert Kirchhoff.⁹ According to Kirchhoff's law, the difference between the enthalpies of a reaction at two different temperatures is just the difference in the enthalpies of heating the products and reactants from T_1 to T_2 . Note that in deriving Equation 7.48 we have assumed that the constant-pressure heat capacities are independent of temperature. Otherwise, they must be expressed as functions of T , and the integral in Equation 7.48 must be done explicitly.

Example 7.15 shows how to use Kirchhoff's law to calculate $\Delta H_{\text{rxn}}^\circ$ for a reaction occurring at a temperature other than 298 K.

Example 7.15

The standard enthalpy change for the reaction



is $-571.6 \text{ kJ mol}^{-1}$ at 25°C . Calculate the value of $\Delta H_{\text{rxn}}^\circ$ at 100°C , assuming that all \bar{C}_P° values are independent of temperature.

—Continued

⁹ Gustav-Robert Kirchhoff (1824–1887). German physicist. Kirchhoff made important contributions to electrical circuit theory, spectroscopy, and thermodynamics. Together with colleague Robert Bunsen (inventor of the Bunsen burner), he codiscovered the elements rubidium and cesium.

Continued—

Strategy We can solve this problem using Kirchhoff's law (Equation 7.49). To do this, though, we need the molar heat capacities, \bar{C}_P° , of the reactants and products, so we can use Equation 7.50 to calculate $\Delta C_{P,\text{rxn}}^\circ$. The molar heat capacity values are listed in Appendix 2.

Solution In Appendix 2, \bar{C}_P° is 29.4, 38.2 J and 75.3 mol⁻¹ K⁻¹ for O₂(g), H₂(g), and H₂O(l), respectively. Using Equation 7.50, we obtain

$$\begin{aligned}\Delta C_{P,\text{rxn}}^\circ &= \sum_{\text{products}} v_p \bar{C}_P^\circ - \sum_{\text{reactants}} v_R \bar{C}_P^\circ \\ &= 2\bar{C}_P^\circ[\text{H}_2\text{O}(l)] - 2\bar{C}_P^\circ[\text{H}_2(g)] - \bar{C}_P^\circ[\text{O}_2(g)] \\ &= 2(75.3 \text{ J mol}^{-1} \text{ K}^{-1}) - 2(28.8 \text{ J mol}^{-1} \text{ K}^{-1}) - 29.4 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 63.8 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

Using Kirchhoff's law (Equation 7.49) gives

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ(T_2) &= \Delta H_{\text{rxn}}^\circ(T_1) + \Delta C_{P,\text{rxn}}^\circ \Delta T \\ &= -571.6 \text{ kJ mol}^{-1} + (63.8 \text{ J mol}^{-1} \text{ K}^{-1})(373.15 \text{ K} - 298.15 \text{ K}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) \\ &= -566.8 \text{ kJ mol}^{-1}\end{aligned}$$

(Heat capacities are generally given in units of J mol⁻¹ K⁻¹, whereas enthalpies are usually in units of kJ mol⁻¹, so we must always be careful to include the conversion from joules to kilojoules in these types of calculations.)

Practice Exercise Using data from Appendix 2, calculate $\Delta H_{\text{rxn}}^\circ$ for the following reaction at 450 K:



Summary of Facts and Concepts

Section 7.1

- ▶ Thermodynamics is the study of energy and its transformations from one form to another in macroscopic systems. Thermochemistry is the study of the energy released or absorbed during chemical reactions.
- ▶ The first law of thermodynamics states that energy is conserved and the change in internal energy of a macroscopic system is the sum of the work done on the system and the energy transferred to the system as heat. In chemistry we are concerned mainly with thermal energy, electrical energy, and mechanical energy, which is usually associated with pressure-volume work.
- ▶ The state of a macroscopic system is defined by a small number of properties such as composition, volume, temperature, and pressure. These properties are called state functions.
- ▶ The change in a state function for a system depends only on the initial and final states of the system, and not on the path by which the change is accomplished. Energy is a state function; work and heat are not.

Section 7.2

- ▶ Enthalpy is a state function. A change in enthalpy ΔH is equal to $\Delta U + \Delta(PV)$, which for a constant-pressure process is equal to $\Delta U + P\Delta V$.
- ▶ The change in enthalpy (ΔH , usually given in kJ) is a measure of the heat absorbed in a process at constant pressure.

Section 7.3

- ▶ The heat capacity of a system tells us how much heat energy must be transferred to a system to achieve a given temperature change.
- ▶ Constant-volume and constant-pressure calorimeters are used to measure heat changes that occur in physical and chemical processes.
- ▶ The equipartition of energy theorem states that the energy in a molecule is, on average, distributed evenly among all molecular degrees of freedom. This theorem can be used to predict the heat capacities of gases.

Section 7.4

- ▶ Hess's law states that the overall enthalpy change in a reaction is equal to the sum of enthalpy changes for individual steps in the overall reaction. Hess's law holds for any extensive thermodynamic quantity.
- ▶ The standard enthalpy of a reaction can be calculated from the standard enthalpies of formation of reactants and products.

Section 7.5

- ▶ The bond enthalpy is the enthalpy change, per mole of gaseous molecules, required to break a particular bond in a molecule. Exact and average bond enthalpies can be used to estimate the standard enthalpy change for reactions.

Key Words

adiabatic process, p. 372
 bond enthalpy, p. 401
 calorimetry, p. 384
 closed system, p. 371
 constant-pressure heat capacity, p. 382
 constant-pressure process, p. 372
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Section 7.6

- ▶ Enthalpy changes also accompany physical transformations such as vaporization, freezing, and sublimation.
- ▶ The heat of solution of an ionic compound in water is the sum of the lattice energy of the compound and the heat of hydration. The relative magnitudes of these two quantities determine whether the solution process is endothermic or exothermic. The heat of dilution is the heat absorbed or evolved when a solution is diluted.

Section 7.7

- ▶ The temperature dependence of reaction enthalpies can be determined from heat capacity data using Kirchhoff's law.

Problems

Thermodynamics Is the Study of Energy and Its Transformations in Macroscopic Systems

- 7.1 A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at constant temperature. Calculate the work done (in joules) if the gas expands (a) against a vacuum, (b) against a constant pressure of 0.80 bar, and (c) against a constant pressure of 3.7 bar.
- 7.2 A gas expands in volume from 26.7 mL to 89.3 mL at constant temperature. Calculate the work done (in joules) if the gas expands (a) against a vacuum, (b) against a constant pressure of 1.5 bar, and (c) against a constant pressure of 2.8 atm.
- 7.3 A gas expands and does $P\text{-}V$ work on the surroundings equal to 325 J. At the same time, it absorbs 127 J

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of heat from the surroundings. Calculate the change in energy of the gas.

- 7.4 Calculate the work done when 50.0 g of tin dissolves in excess acid at 1.00 bar and 25°C



Assume ideal gas behavior.

- 7.5 Calculate the work done (in joules) when 1.0 mole of water vaporizes at 1.0 atm and 100°C. Assume ideal gas behavior and that the volume of liquid water is negligible compared with that of steam at 100°C.
- 7.6 Show that the work required for the reversible and isothermal expansion of n moles of a van der Waals

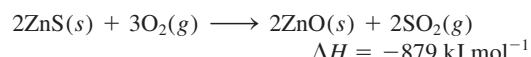
gas (Equation 5.42) from an initial volume V_1 to a final volume V_2 is given by

$$w = nRT \ln \frac{V_1 - nb}{V_2 - nb} + an^2 \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

- 7.7 Using the result from Problem 7.6, calculate the work required to compress 10.0 moles of CO_2 from a volume of 2500 L to 100 L at a fixed temperature of 298 K. The van der Waals parameters a and b for carbon dioxide can be found in Table 5.3. Compare this to the value obtained assuming that CO_2 behaves ideally. What does the difference between these two predictions tell you about the relative importance of attractive and repulsive molecular interactions in CO_2 under these conditions?
- 7.8 If energy is conserved, how can there be an energy crisis?

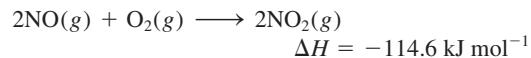
Energy Absorbed by a System as Heat in a Constant-Pressure Process Is Equal to Change in Enthalpy

- 7.9 The first step in the industrial recovery of zinc from the zinc sulfide ore is roasting—that is, the conversion of ZnS to ZnO by heating:

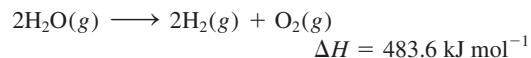


Calculate the heat evolved (in kJ) per gram of ZnS roasted.

- 7.10 Determine the amount of heat (in kJ) given off when 1.26×10^4 g of NO_2 are produced according to the equation



- 7.11 Consider the reaction



If 2.0 moles of $\text{H}_2\text{O}(g)$ are converted to $\text{H}_2(g)$ and $\text{O}_2(g)$ against a pressure of 1.0 bar at 125°C, what is ΔU for this reaction?

- 7.12 Consider the reaction



If 3.0 moles of H_2 react with 3.0 moles of Cl_2 to form HCl , calculate the work done (in joules) against a pressure of 1.0 bar at 25°C. What is ΔU for this reaction? Assume the reaction goes to completion.

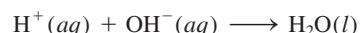
The Temperature Change of a System Upon Heating Is Governed by Its Heat Capacity

- 7.13 A 6.22-kg slab of copper metal is heated from 20.5°C to 324.3°C. Calculate the heat absorbed (in kJ) by the metal.
- 7.14 Calculate the amount of heat liberated (in kJ) from 366 g of mercury when it cools from 77.0°C to 12.0°C.

- 7.15 A sheet of gold weighing 10.0 g and at a temperature of 18.0°C is placed flat on a sheet of iron weighing 20.0 g and at a temperature of 55.6°C. What is the final temperature of the combined metals? Assume that no heat is lost to the surroundings. (*Hint:* The heat gained by the gold must be equal to the heat lost by the iron. The specific heat capacities of the metals are given in Table 7.1.)

- 7.16 A 40.0-g sample of copper at 200°C is dropped into a well-insulated vessel containing 100.0 g of H_2O initially at 25°C. Calculate the final temperature of the system given that the specific heat capacity of water is $4.184 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ and the specific heat capacity of copper is $0.385 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$.
- 7.17 A 0.1375-g sample of solid magnesium is burned in a constant-volume bomb calorimeter that has a heat capacity of $3024 \text{ J }^\circ\text{C}^{-1}$. The temperature increases by 1.126°C. Calculate the heat given off by the burning Mg, both in kJ g^{-1} and in kJ mol^{-1} .

- 7.18 A quantity of 2.00×10^2 mL of 0.862 M HCl is mixed with 2.00×10^2 mL of 0.431 M Ba(OH)_2 in a constant-pressure calorimeter of negligible heat capacity. The initial temperatures of the HCl and Ba(OH)_2 solutions are both 20.48°C. The heat of neutralization is 56.2 kJ mol⁻¹ for



What is the final temperature of the mixed solution?

- 7.19 Determine the equipartition predictions for the heat capacities of CO , N_2O , O_3 , and H_2CO both including and excluding the vibrational contribution. Compare these to the experimental values at 25°C. How important are the vibrational contributions in each case?
- 7.20 The average temperature in deserts is high during the day but quite cool at night, whereas that in regions along the coastline is more moderate. Explain.

The Enthalpy Change for Any Reaction Can Be Calculated Using Standard Enthalpies of Formation

- 7.21 Which is the more negative quantity at 25°C: ΔH_f° for $\text{H}_2\text{O}(l)$ or ΔH_f° for $\text{H}_2\text{O}(g)$?
- 7.22 Predict the value of ΔH_f° (greater than, less than, or equal to zero) for the following elements at 25°C: (a) $\text{Br}_2(g)$, $\text{Br}_2(l)$; and (b) $\text{I}_2(g)$, $\text{I}_2(s)$.
- 7.23 In general, compounds with negative ΔH_f° values are more stable than those with positive ΔH_f° values. $\text{H}_2\text{O}_2(l)$ has a negative ΔH_f° (see Table 7.5). Why, then, does $\text{H}_2\text{O}_2(l)$ have a tendency to decompose to $\text{H}_2\text{O}(l)$ and $\text{O}_2(g)$?
- 7.24 Suggest ways (with appropriate equations) that would allow you to measure the ΔH_f° values of $\text{Ag}_2\text{O}(s)$ and $\text{CaCl}_2(s)$ from their elements. No calculations are necessary.

- 7.25 Calculate the heat of decomposition for the following process at constant pressure and 25°C:



(Hint: You can find the standard enthalpy of formation of the reactant and products in Table 7.5.)

- 7.26 The standard enthalpies of formation of ions in aqueous solutions are obtained by arbitrarily assigning a value of zero to H⁺ ions, that is, ΔH_f[°][H^{+(aq)}] = 0.

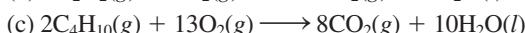
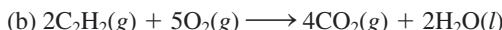
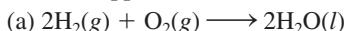
(a) For the following reaction



calculate ΔH_f[°] for the Cl⁻ ions.

(b) Given that ΔH_f[°] for OH⁻ ions is -229.6 kJ mol⁻¹, calculate the enthalpy of neutralization when 1 mole of a strong monoprotic acid (such as HCl) is neutralized by 1 mole of a strong base (such as KOH) at 25°C. Assume complete neutralization.

- 7.27 Calculate the heats of combustion for the following reactions from the standard enthalpies of formation listed in Appendix 2:



- 7.28 Calculate the heats of combustion for the following reactions from the standard enthalpies of formation listed in Appendix 2:



- 7.29 Methanol, ethanol, and *n*-propanol are three common alcohols. When 1.00 g of each of these alcohols is burned in air, heat is liberated as shown by the following data: (a) methanol (CH₃OH), -22.6 kJ; (b) ethanol (C₂H₅OH), -29.7 kJ; and (c) *n*-propanol (C₃H₇OH), -33.4 kJ. Calculate the heats of combustion of these alcohols in kJ mol⁻¹.

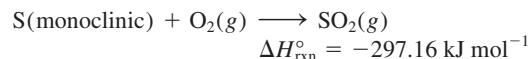
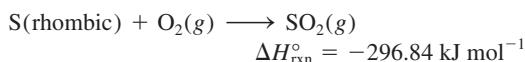
- 7.30 The standard enthalpy change for the following reaction is 436.4 kJ mol⁻¹:



Calculate the standard enthalpy of formation of atomic hydrogen (H).

- 7.31 At 850°C, CaCO₃ undergoes substantial decomposition to yield CaO and CO₂. Assuming that the ΔH_f[°] values of the reactant and products are the same at 850°C as they are at 25°C, calculate the enthalpy change (in kJ) if 66.8 g of CO₂ is produced in one reaction.

- 7.32 From these data,

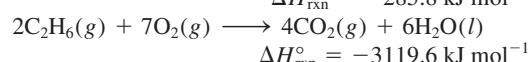
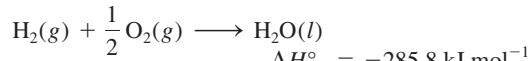
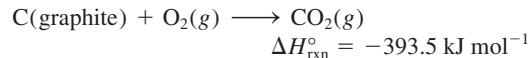


calculate the enthalpy change for the transformation



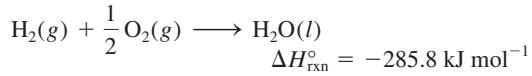
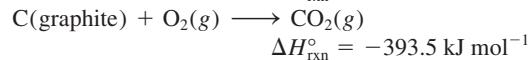
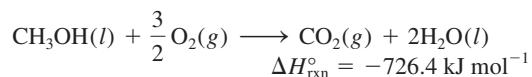
(Monoclinic and rhombic are different allotropic forms of elemental sulfur.)

- 7.33 From the following data,



calculate the enthalpy change for the reaction 2C(graphite) + 3H₂(g) → C₂H₆(g).

- 7.34 From the following heats of combustion,



calculate the standard enthalpy of formation of methanol (CH₃OH) from its elements.

- 7.35 The convention of arbitrarily assigning a zero enthalpy value for the most stable form of each element in the standard state at 25°C is a convenient way of dealing with enthalpies of reactions. Explain why this convention cannot be applied to nuclear reactions.

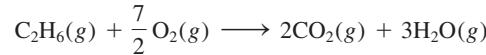
The Reaction Enthalpies Can Be Estimated from Bond Enthalpies

- 7.36 Explain why the bond enthalpy of a molecule is always defined in terms of a gas-phase reaction.

- 7.37 The bond enthalpy of F₂ is 150.6 kJ mol⁻¹. Calculate the value of ΔH_f[°] for F(g).

- 7.38 Use the bond enthalpy data in Table 7.6 to calculate the enthalpies of formation of the following gases: (a) H₂O(g), (b) NH₃, (c) H₂O₂, (d) H₂NCl.

- 7.39 Use the bond enthalpy values in Table 7.6 to calculate the enthalpy of combustion for ethane (C₂H₆):



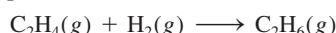
- 7.40 Alkanes are hydrocarbons with the general formula C_nH_{2n+2}, where *n* is a positive integer. Using the data from Table 7.6, derive general formulas for the enthalpies of combustion (in kJ g⁻¹) for gas-phase alkanes as functions of *n*.

Enthalpy Changes Also Accompany Physical Transformations

- 7.41 Calculate the amount of heat (in kJ) required to convert 74.6 g of water to steam at 100°C.
- 7.42 How much heat (in kJ) is needed to convert 866 g of ice at –10°C to steam at 126°C? (The specific heat capacities of ice and steam are 2.03 and 1.99 J g^{–1} °C^{–1}, respectively.)
- 7.43 The molar enthalpies of fusion and sublimation of molecular iodine are 15.27 and 62.30 kJ mol^{–1}, respectively. Estimate the molar heat of vaporization of liquid iodine.
- 7.44 The molar enthalpies of fusion and vaporization of water at 298 K are 6.01 and 44.01 kJ mol^{–1}, respectively. Use these values to estimate the molar enthalpy of sublimation of ice.
- 7.45 The enthalpy of vaporization is found to decrease with increasing temperature for a certain substance. What information does this give you about the relative properties of the liquid and vapor phases?

The Temperature Dependence of Reaction Enthalpies Can Be Determined from Heat Capacity Data

- 7.46 The hydrogenation of ethylene is given by the following equation:



Using data from Appendix 2, calculate the change in the enthalpy of hydrogenation from 298 K to 398 K. Assume the heat capacities are temperature independent.

- 7.47 Use the data in Appendix 2 to calculate the value of $\Delta H_{\text{rxn}}^\circ$ for the following reaction at 298 K:

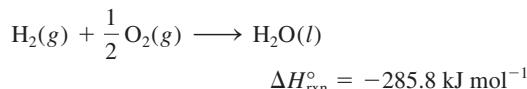


What is its value at 350 K? State any assumptions in your calculation.

- 7.48 The heat of fusion of ice at the standard melting point (0°C) is 6.01 kJ mol^{–1}. Determine the heat of fusion at –10°C using data from Appendix 2.

Additional Problems

- 7.49 From the enthalpy of vaporization of water at its standard boiling point and the bond enthalpies of H₂ and O₂, calculate the average O—H bond energy in liquid water, given that



- 7.50 Calculate the fraction of the enthalpy of vaporization of water used for the expansion of steam at its standard boiling point.

- 7.51 The combustion of what volume of ethane (C₂H₆), measured at 23.0°C and 752 mm Hg, would be

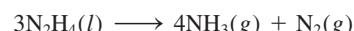
required to heat 855 g of water from 25.0°C to 98.0°C?

- 7.52 The standard enthalpy change ($\Delta H_{\text{rxn}}^\circ$) for the thermal decomposition of silver nitrate according to the following equation is 78.67 kJ mol^{–1}:



The standard enthalpy of formation of AgNO₃(s) is –123.02 kJ mol^{–1}. Calculate the standard enthalpy of formation of AgNO₂(s).

- 7.53 Hydrazine (N₂H₄) decomposes according to the following equation:



(a) Given that the standard enthalpy of formation of hydrazine is 50.63 kJ mol^{–1}, calculate $\Delta H_{\text{rxn}}^\circ$ for its decomposition. (b) Both hydrazine and ammonia burn in oxygen to produce H₂O(l) and N₂(g). Write balanced equations for each of these processes and calculate $\Delta H_{\text{rxn}}^\circ$ for each of them. On a mass basis (per kg), would hydrazine or ammonia be the better fuel?

- 7.54 Consider the equation



If 2.0 moles of N₂ react with 6.0 moles of H₂ to form NH₃, calculate the work done (in joules) against a pressure of 1.0 bar at 25°C. What is ΔU° for this reaction? Assume the reaction goes to completion.

- 7.55 Calculate the heat released when 2.00 L of Cl₂(g) (density = 1.88 g L^{–1}) reacts with an excess of sodium metal as 25°C and 1 bar to form sodium chloride.

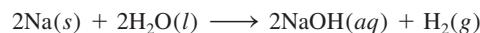
- 7.56 Photosynthesis produces glucose (C₆H₁₂O₆) and oxygen from carbon dioxide and water:



(a) How would you determine experimentally the $\Delta H_{\text{rxn}}^\circ$ value for this reaction? (b) Solar radiation produces about 7.0×10^{14} kg of glucose a year on Earth. What is the corresponding ΔH° change?

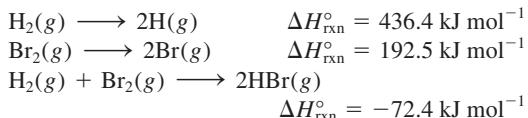
- 7.57 A 2.10-mole sample of crystalline acetic acid, initially at 17.0°C, is allowed to melt at 17.0°C and is then heated to 118.1°C (its normal boiling point) at 1.00 atm. The sample is allowed to vaporize at 118.1°C and is then rapidly quenched to 17.0°C, so that it recrystallizes. Calculate ΔH° for the total process as described.

- 7.58 Calculate the work done in joules by the following equation:

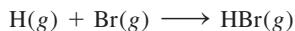


when 0.34 g of Na reacts with water to form hydrogen gas at 0°C and 1.0 bar.

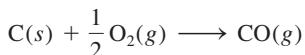
- 7.59 You are given the following data:



Calculate $\Delta H_{\text{rxn}}^\circ$ for the reaction



- 7.60 A 44.0-g sample of an unknown metal at 99.0°C was placed in a constant-pressure calorimeter containing 80.0 g of water at 24.0°C. The final temperature of the system was found to be 28.4°C. Calculate the specific heat capacity of the metal. (The heat capacity of the calorimeter is 12.4 J °C⁻¹.)
- 7.61 A 1.00-mole sample of ammonia at 14.0 bar and 25°C in a cylinder fitted with a movable piston expands against a constant external pressure of 1.00 bar. At equilibrium, the pressure and volume of the gas are 1.00 bar and 23.5 L, respectively. (a) Calculate the final temperature of the sample. (b) Calculate q , w , and ΔU for the process. The specific heat capacity of ammonia is 0.0258 J g °C⁻¹.
- 7.62 Producer gas (carbon monoxide) is prepared by passing air over red-hot coke:

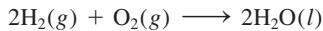


Water gas (a mixture of carbon monoxide and hydrogen) is prepared by passing steam over red-hot coke:



For many years, both producer gas and water gas were used as fuels in industry and for domestic cooking. The large-scale preparation of these gases was carried out alternately, that is, first producer gas, then water gas, and so on. Using thermochemical reasoning, explain why this procedure was chosen.

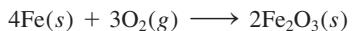
- 7.63 Compare the heat produced by the complete combustion of 1.00 mole of methane (CH_4) with 1.00 mol of water gas (0.50 mol H_2 and 0.50 mol CO) under the same conditions. On the basis of your answer, would you prefer methane over water gas as a fuel? Can you suggest two other reasons why methane is preferable to water gas as a fuel?
- 7.64 The so-called hydrogen economy is based on hydrogen produced from water using solar energy. The gas is then burned as a fuel:



A primary advantage of hydrogen as a fuel is that it is nonpolluting. A major disadvantage is that it is a

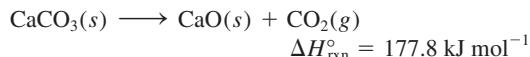
gas and therefore is harder to store than liquids or solids. Calculate the volume of hydrogen gas at 25°C and 1.00 bar required to produce an amount of energy equivalent to that produced by the combustion of a liter of octane (C_8H_{18}). The density of octane is 2.66 kg gal⁻¹, and its standard enthalpy of formation is $-249.9 \text{ kJ mol}^{-1}$.

- 7.65 Ethanol ($\text{C}_2\text{H}_5\text{OH}$) and gasoline [assumed to be all octane (C_8H_{18})] are both used as automobile fuel. If gasoline is selling for \$3.00 per gal, what would the price of ethanol have to be in order to provide the same amount of heat per dollar? The density and ΔH_f° of octane are 0.7025 g mL^{-1} and $-249.9 \text{ kJ mol}^{-1}$, respectively, and of ethanol are 0.7894 g mL^{-1} and $-277.0 \text{ kJ mol}^{-1}$, respectively. (1 gal = 3.785 L.)
- 7.66 The molar enthalpy of vaporization of a liquid (ΔH_{vap}) is the energy required to vaporize 1.00 mol of the liquid. In one experiment, 60.0 g of liquid nitrogen (boiling point -196°C) is poured into a Styrofoam cup containing $2.00 \times 10^2 \text{ g}$ of water at 55.3°C . Calculate the molar enthalpy of vaporization of liquid nitrogen if the final temperature of the water is 41.0°C .
- 7.67 A quantity of 0.020 mole of a gas initially at 0.050 L and 20°C undergoes a constant-temperature expansion until its volume is 0.50 L. Calculate the work done (in joules) by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 0.20 bar. (c) If the gas in (b) is allowed to expand unchecked until its pressure is equal to the external pressure, what would its final volume be before it stopped expanding, and what would be the work done?
- 7.68 (a) For most efficient use, refrigerator freezer compartments should be fully packed with food. What is the thermochemical basis for this recommendation? (b) Starting at the same temperature, tea and coffee remain hot longer in a thermal flask than chicken noodle soup. Explain.
- 7.69 Portable hot packs are available for skiers and people engaged in other outdoor activities in a cold climate. The air-permeable paper packet contains a mixture of powdered iron, sodium chloride, and other components, all moistened by a little water. The exothermic reaction that produces the heat (the rusting of iron) is

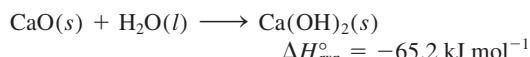


When the outside plastic envelope is removed, O_2 molecules penetrate the paper, causing the reaction to begin. A typical packet contains 250 g of iron to warm your hands or feet for up to 4 hours. How much heat (in kJ) is produced by this reaction? (Hint: See Appendix 2 for ΔH_f values.)

- 7.70 A man ate 0.50 pound of cheese (an energy intake of 4000 kJ). Suppose that none of the energy was stored in his body. What mass (in grams) of water would he need to perspire in order to maintain his original temperature? (It takes 44.0 kJ of heat to vaporize 1 mole of water.)
- 7.71 The total volume of the Pacific Ocean is estimated to be $7.2 \times 10^8 \text{ km}^3$. A medium-sized atomic bomb produces $1.0 \times 10^{15} \text{ J}$ of energy upon explosion. Calculate the number of atomic bombs needed to release enough energy to raise the temperature of the water in the Pacific Ocean by 1°C .
- 7.72 A 19.2-g quantity of dry ice (solid carbon dioxide) is allowed to sublime in an apparatus like the one shown in Figure 7.2. Calculate the expansion work done against a constant external pressure of 0.995 bar and at a constant temperature of 22°C . Assume that the initial volume of dry ice is negligible and that CO_2 behaves like an ideal gas.
- 7.73 The enthalpy of combustion of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) is commonly used as the standard for calibrating constant-volume bomb calorimeters; its value has been accurately determined to be $-3226.7 \text{ kJ mol}^{-1}$. When 1.9862 g of benzoic acid are burned in a calorimeter, the temperature rises from 21.84°C to 25.67°C . What is the heat capacity of the bomb? (Assume that the quantity of water surrounding the bomb is exactly 2000 g.)
- 7.74 *Lime* is a term that includes calcium oxide (CaO , also called quicklime) and calcium hydroxide [$\text{Ca}(\text{OH})_2$, also called slaked lime]. It is used in the steel industry to remove acidic impurities, in air-pollution control to remove acidic oxides such as SO_2 , and in water treatment. Quicklime is made industrially by heating limestone (CaCO_3) above 2000°C :



Slaked lime is produced by treating quicklime with water:



The exothermic reaction of quicklime with water and the rather small specific heats of both quicklime ($0.946 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$) and slaked lime ($1.20 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$) make it hazardous to store and transport lime in vessels made of wood. Wooden sailing ships carrying lime would occasionally catch fire when water leaked into the hold. (a) If a 500-g sample of water reacts with an equimolar amount of CaO (both at an initial temperature of 25°C), what is the final temperature of the product, $\text{Ca}(\text{OH})_2$? Assume that the product absorbs all the heat released in the reaction. (b) Given that the standard enthalpies of formation of CaO and H_2O are -635.6 and $-285.8 \text{ kJ mol}^{-1}$, respectively,

calculate the standard enthalpy of formation of $\text{Ca}(\text{OH})_2$.

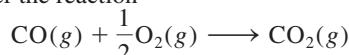
- 7.75 Calcium oxide (CaO) is used to remove sulfur dioxide generated by coal-burning power stations: $2\text{CaO}(s) + 2\text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2\text{CaSO}_4(s)$. Calculate the enthalpy change for this process if $6.6 \times 10^5 \text{ g}$ of SO_2 are removed by this process every day.
- 7.76 Glauber's salt, sodium sulfate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), undergoes a phase transition (that is, melting or freezing) at a convenient temperature of about 32°C
- $$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}(s) \longrightarrow \text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}(l)$$
- $$\Delta H_{\text{rxn}}^\circ = 74.4 \text{ kJ mol}^{-1}$$
- As a result, this compound is used to regulate the temperature in homes. It is placed in plastic bags in the ceiling of a room. During the day, the endothermic melting process absorbs heat from the surroundings, cooling the room. At night, it gives off heat as it freezes. Calculate the mass of Glauber's salt in kilograms needed to lower the temperature of air in a room by 8.2°C at 1.0 bar. The dimensions of the room are $2.80 \text{ m} \times 10.6 \text{ m} \times 17.2 \text{ m}$, the specific heat of air is $1.2 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$, and the molar mass of air may be taken as 29.0 g mol^{-1} .
- 7.77 A balloon 16 m in diameter is inflated with helium at 18°C . (a) Calculate the mass of He in the balloon, assuming ideal behavior. (b) Calculate the work done (in joules) during the inflation process if the atmospheric pressure is 98.7 kPa.
- 7.78 An excess of zinc metal is added to 50.0 mL of a 0.100 M AgNO_3 solution in a constant-pressure calorimeter like the one depicted in Figure 7.12. As a result of the reaction
- $$\text{Zn}(s) + 2\text{Ag}^+(aq) \longrightarrow \text{Zn}^{2+}(aq) + 2\text{Ag}(s)$$
- the temperature rises from 19.25°C to 22.17°C . If the heat capacity of the calorimeter is $98.6 \text{ J }^\circ\text{C}^{-1}$, calculate the enthalpy change for this reaction on a molar basis. Assume that the density and specific heat capacity of the solution are the same as those for water, and ignore the specific heat capacities of the metals.
- 7.79 (a) A person drinks four glasses of cold water (3.0°C) every day. The volume of each glass is $2.5 \times 10^2 \text{ mL}$. How much heat (in kJ) does the body have to supply to raise the temperature of the water to 37°C (the normal body temperature)? (b) How much heat would your body lose if you were to ingest $8.0 \times 10^2 \text{ g}$ of snow at 0°C to quench your thirst? (The amount of heat necessary to melt snow is 6.01 kJ mol^{-1} .)
- 7.80 Equal amounts of heat are added to two containers. One contains 1.0 mol of carbon dioxide and the other contains 1.0 mol of ammonia. If both are originally at the same temperature, which container (if any) will have the higher temperature at the end? Use molecular reasoning to justify your answer.

- 7.81 A driver's manual states that the stopping distance quadruples as the speed (u) doubles, that is, if it takes 30 ft to stop a car moving at 25 mph, then it would take 120 ft to stop a car moving at 50 mph. Justify this statement by using mechanics and the first law of thermodynamics. (Assume that when a car is stopped, its kinetic energy ($mu^2/2$) is completely converted to heat.)
- 7.82 At 25°C the standard enthalpy of formation of HF(*aq*) is 320.1 kJ mol⁻¹; of OH⁻(*aq*), it is -229.6 kJ mol⁻¹; of F⁻(*aq*), it is -329.1 kJ mol⁻¹; and of H₂O(*l*), it is -285.8 kJ mol⁻¹. (a) Calculate the standard enthalpy of neutralization of HF(*aq*):
- $$\text{HF}(aq) + \text{OH}^-(aq) \longrightarrow \text{F}^-(aq) + \text{H}_2\text{O}(l)$$
- (b) Using the value of -56.2 kJ mol⁻¹ as the standard enthalpy change for the reaction
- $$\text{H}^+(aq) + \text{OH}^-(aq) \longrightarrow \text{H}_2\text{O}(l)$$
- calculate the standard enthalpy change for the reaction
- $$\text{HF}(aq) \longrightarrow \text{H}^+(aq) + \text{F}^-(aq)$$
- 7.83 Why are cold, damp air and hot, humid air more uncomfortable than dry air at the same temperatures? (The specific heat capacities of water vapor and air are approximately 1.9 and 1.0 J g⁻¹ °C⁻¹, respectively.)
- 7.84 A 46-kg person drinks 500 g of milk, which has a "caloric" value of approximately 3.0 kJ g⁻¹. If only 17 percent of the energy in milk is converted to mechanical work, how high (in meters) can the person climb based on this energy intake? [Hint: The work done in ascending is given by mgh , where m is the mass (in kg), g is the gravitational acceleration (9.8 m s⁻²), and h is the height (in meters).]
- 7.85 The height of Niagara Falls on the American side is 51 m. (a) Calculate the potential energy of 1.0 g of water at the top of the falls relative to the ground level. (b) What is the speed of the falling water if all the potential energy is converted to kinetic energy? (c) What would be the increase in temperature of the water if all the kinetic energy were converted to heat? (See the Problem 7.84 for suggestions.)
- 7.86 In early 2005, the European Space Agency's Huygens Probe landed on Saturn's largest moon Titan. Soon after the 319-kg probe impacted the surface at a speed of 5 m s⁻¹, a sudden increase in methane gas concentration was detected. The methane is believed to have been produced by the conversion of liquid methane in the soil to vapor as a result of heating from the impact. Determine the maximum amount of liquid methane that could have been evaporated in this process. State any assumptions that you make.
- 7.87 In the nineteenth century two scientists named Dulong and Petit noticed that for a solid element, the product of its molar mass and its specific heat capacity is approximately 25 J °C⁻¹. This observation, now called Dulong and Petit's law, was used to estimate the specific heat capacity of metals. Verify the law for the metals listed in Table 7.1. The law does not apply to one of the metals. Which one is it? Why?
- 7.88 Determine the standard enthalpy of formation of ethanol (C₂H₅OH) from its standard enthalpy of combustion (-1367.4 kJ mol⁻¹).
- 7.89 Acetylene (C₂H₂) and benzene (C₆H₆) have the same empirical formula. In fact, benzene can be made from acetylene as follows:
- $$3\text{C}_2\text{H}_2(g) \longrightarrow \text{C}_6\text{H}_6(l)$$
- The enthalpies of combustion for C₂H₂ and C₆H₆ are -1299.4 kJ mol⁻¹ and -3267.4 kJ mol⁻¹, respectively. Calculate the standard enthalpies of formation of C₂H₂ and C₆H₆ and hence the enthalpy change for the formation of C₆H₆ from C₂H₂.
- 7.90 Ice at 0°C is placed in a Styrofoam cup containing 361 g of a soft drink at 23°C. The specific heat of the drink is about the same as that of water. Some ice remains after the ice and soft drink reach an equilibrium temperature of 0°C. Determine the mass of ice that has melted. Ignore the heat capacity of the cup. (Hint: It takes 334 J to melt 1 g of ice at 0°C.)
- 7.91 A gas company in Massachusetts charges \$1.30 for 15 ft³ of natural gas (CH₄) measured at 20°C and 1.0 bar. Calculate the cost of heating 200 mL of water (enough to make a cup of coffee or tea) from 20°C to 100°C. Assume that only 50 percent of the heat generated by the combustion is used to heat the water; the rest of the heat is lost to the surroundings.
- 7.92 Suppose 100 g of Al metal at 250°C is added to 100 g of ice at -15°C. Assuming no heat is lost to the surroundings, determine (a) the final temperature and (b) the amounts of each phase present.
- 7.93 Calculate the internal energy of a Goodyear blimp filled with helium gas at 1.2 × 10⁵ Pa. The volume of the blimp is 5.5 × 10³ m³. If all the energy were used to heat 10.0 tons of copper at 21°C, calculate the final temperature of the metal (1 ton = 9.072 × 10⁵ g).
- 7.94 Decomposition reactions are usually endothermic, whereas combination reactions are usually exothermic. Give a qualitative explanation for these trends.
- 7.95 Acetylene (C₂H₂) can be made by reacting calcium carbide (CaC₂) with water. (This reaction was once employed in lamps used in cave exploration.) (a) Write an equation for the reaction. (b) What is the maximum amount of heat (in joules) that can be obtained from the combustion of acetylene, starting with 74.6 g of CaC₂?

7.96 When 1.034 g of naphthalene ($C_{10}H_8$) is burned in a constant-volume bomb calorimeter at 298 K, 41.56 kJ of heat is evolved. Calculate ΔU and ΔH for the reaction on a molar basis.

7.97 From a thermochemical point of view, explain why a carbon dioxide fire extinguisher or water should not be used on a magnesium fire.

7.98 Consider the reaction



Without doing any calculation and basing your answer on molecular considerations alone, will the enthalpy change for this reaction increase or decrease with increasing temperature?

7.99 A 4.117-g impure sample of glucose ($C_6H_{12}O_6$) was burned in a constant-volume calorimeter having a heat capacity of $19.65 \text{ kJ } ^\circ\text{C}^{-1}$. If the rise in temperature is 3.134°C , calculate the percent by mass of the glucose in the sample. Assume that the impurities are unaffected by the combustion process. See Appendix 2 for thermodynamic data.

7.100 Construct a table with the headings q , w , ΔU , and ΔH . For each of the following processes, deduce whether each of the quantities listed is positive (+), negative (-), or zero. (a) Freezing of benzene. (b) Compression of an ideal gas at constant temperature. (c) Reaction of sodium with water. (d) Boiling liquid ammonia. (e) Heating a gas at constant volume. (f) Melting of ice.

7.101 The combustion of 0.4196 g of a hydrocarbon releases 17.55 kJ of heat. The masses of the products are $CO_2 = 1.419 \text{ g}$ and $H_2O = 0.290 \text{ g}$. (a) What is the empirical formula of the compound? (b) If the approximate molar mass of the compound is 76 g, calculate its standard enthalpy of formation.

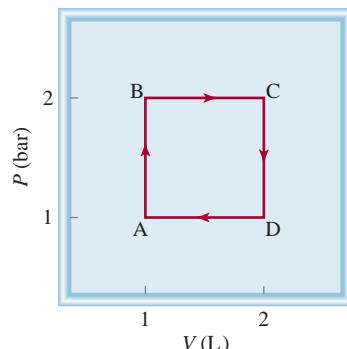
7.102 Metabolic activity in the human body releases approximately $1.0 \times 10^4 \text{ kJ}$ of heat per day. Assuming the body contains 50 kg of water, how much would the body temperature rise if it were an isolated system? How much water must the body eliminate as perspiration to maintain the normal body temperature (37.0°C)? Comment on your results. The heat of vaporization of water is 2.41 kJ g^{-1} .

7.103 For a diatomic molecule, the vibrational contribution to the heat capacity can be calculated using statistical mechanics, assuming that the vibrations are well modeled by a harmonic oscillator:

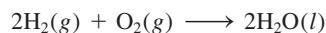
$$\bar{C}_V(\text{vibration}) = \frac{\Theta_v^2}{T^2} \left(\frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/2T}} \right)^2 R$$

The quantity $\Theta_v = hc\bar{v}/k$ is called the *vibrational temperature*, where h is Planck's constant, c is the speed of light, k is Boltzmann's constant, and \bar{v} is the vibrational frequency in wave numbers (cm^{-1}). The vibrational frequencies for F_2 and I_2 are 919 and 214 cm^{-1} , respectively. Use the formula above, together with the equipartition values for the translational and rotational contributions, to calculate the constant-pressure heat capacity for these two diatomic molecules. Compare your results with the experimental values given in Table 7.4.

7.104 Starting at A, an ideal gas undergoes a cyclic process involving expansion and compression at constant temperature as shown. Calculate the total work done. Does your result support the notion that work is not a state function?



7.105 Calculate the ΔU for the following reaction at 298 K



7.106 From the following data, calculate the heat of solution for KI:

| | NaCl | NaI | KCl | KI |
|---|------|------|------|-----|
| Lattice energy (kJ mol^{-1}) | 788 | 686 | 699 | 632 |
| Heat of solution (kJ mol^{-1}) | 4.0 | -5.1 | 17.2 | ? |

Answers to Practice Exercises

7.1 (a) 0; (b) 283 J **7.2** $w = 1.11 \text{ kJ}$; $q = -1.11 \text{ kJ}$; $\Delta U = 0$
7.3 $-6.47 \times 10^3 \text{ kJ}$ **7.4** $-111.7 \text{ kJ mol}^{-1}$ **7.5** $\Delta U = 693 \text{ J}$;
 $\Delta H = 893 \text{ J}$ **7.6** -728 kJ mol^{-1} **7.7** 21.19°C **7.8** 22.49°C

7.9 $3.0 \text{ J mol}^{-1} \text{ K}^{-1}$; 9.3% **7.10** 87.3 kJ mol^{-1} **7.11** 40.1 kJ g^{-1}
7.12 (a) $-543.1 \text{ kJ mol}^{-1}$; (b) $-543.2 \text{ kJ mol}^{-1}$ **7.13** (a)
 -119 kJ mol^{-1} ; (b) -137 kJ mol^{-1} **7.14** $-57.60 \text{ kJ mol}^{-1}$

8

Chapter

Entropy, Free Energy, and the Second Law of Thermodynamics



According to the first law of thermodynamics (Chapter 7), energy can be neither created nor destroyed, but flows from one part of the universe to another or is converted from one form to another. The total amount of energy in the universe remains constant. Despite its immense value in the study of energy changes in chemical reactions, the first law is still limited because it cannot predict the direction of change. It helps us to do the bookkeeping of energy balance, such as the energy input, energy released, and work done, but it reveals nothing about whether a particular process can indeed occur. For this kind of information, we must turn to the second law of thermodynamics and the concept of entropy.

- 8.1** The Entropy of an Isolated System Always Increases in Any Spontaneous Process 424
- 8.2** The Entropy Change for a Process Can Be Calculated Using the Thermodynamic Definition of Entropy 432
- 8.3** The Third Law of Thermodynamics Allows Us to Determine Absolute Entropies 440
- 8.4** The Spontaneity of a Process at Constant Temperature and Pressure Is Governed by the Gibbs Free Energy 446
- 8.5** The Mixing of Pure Substances Leads to an Increase in the Entropy and a Decrease in the Gibbs Free Energy 456
- 8.6** In Living Systems, Spontaneous Reactions Are Used to Drive Other Nonspontaneous, but Essential, Biochemical Processes 459

8.1 | The Entropy of an Isolated System Always Increases in Any Spontaneous Process

One of the main objectives in studying thermodynamics, as far as chemists are concerned, is to be able to predict whether or not a process or reaction will occur under a specific set of conditions (such as temperature, pressure, and concentration). This knowledge is useful whether we are synthesizing compounds in a research laboratory, manufacturing chemicals on an industrial scale, or trying to understand the intricate biological processes in a cell.

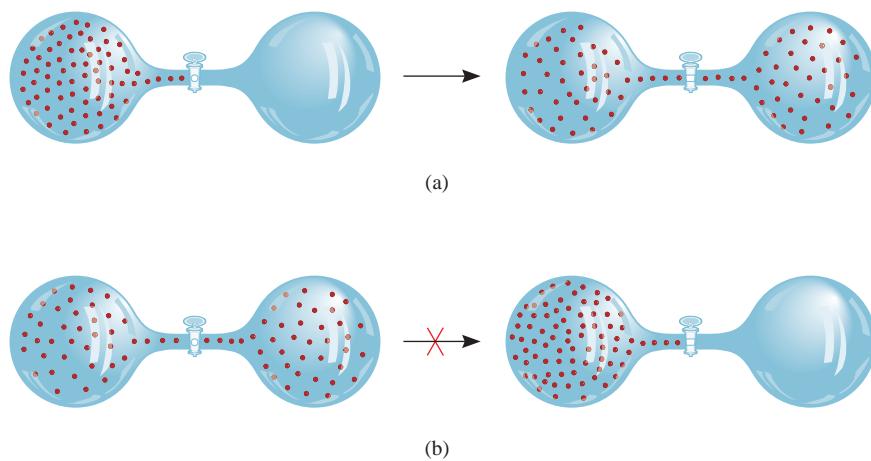
Spontaneous Processes

A *spontaneous process* occurs without external intervention under the given set of conditions. A process is *nonspontaneous* if it does *not* occur without external intervention under the specified set of conditions.

We observe spontaneous physical and chemical processes every day. For example, a lump of sugar when placed in hot coffee will dissolve on its own. Because no external intervention is required to make the sugar dissolve, this is a spontaneous process. The reverse process—precipitation of the sugar from the hot coffee—is non-spontaneous. It will never occur—no matter how long you wait. *In general, processes that occur spontaneously in one direction cannot, under the same conditions, also take place spontaneously in the reverse direction.* Other examples of spontaneous processes include the following:

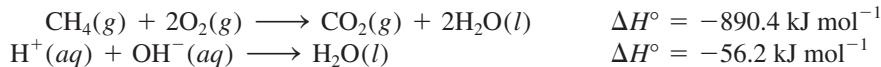
- ▶ Heat flows from a hotter object to a colder one, but the reverse never happens spontaneously.
- ▶ The expansion of a gas into an evacuated bulb is spontaneous [Figure 8.1(a)], but the reverse process (the concentration of all the molecules into one bulb) is nonspontaneous [Figure 8.1(b)].
- ▶ A piece of sodium metal reacts violently with water to form sodium hydroxide and hydrogen gas, but hydrogen gas does not react with sodium hydroxide to form water and sodium metal.
- ▶ Iron exposed to water and oxygen forms rust, but rust does not spontaneously change back to iron.

Figure 8.1 (a) A spontaneous process. (b) A nonspontaneous process—the reverse of (a).



The term *spontaneous* says nothing about the speed with which a process takes place—only that it will take place *if given enough time*. For example, it may take days or weeks for wet iron to rust, but the process is still spontaneous.

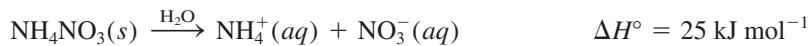
If we assume that spontaneous processes occur so as to decrease the energy of a system, we can explain why a ball rolls downhill and why springs in a clock unwind. Similarly, many exothermic reactions are spontaneous, such as the combustion of methane and acid-base neutralization reactions:



However, consider a solid-to-liquid phase transition such as the melting of ice,



It is spontaneous above 0°C even though the process is endothermic. Another process that is spontaneous, as well as endothermic, is dissolution of ammonium nitrate in water,



The decomposition of mercury(II) oxide is endothermic and nonspontaneous at room temperature, but it becomes spontaneous when the temperature is raised:



Based on these examples and many others, the most we can conclude is that exothermicity *favors* the spontaneity of a reaction but does *not* guarantee it. Just as it is possible for an endothermic reaction to be spontaneous, an exothermic reaction can be nonspontaneous. In other words, we cannot determine whether a chemical reaction will occur spontaneously solely on the basis of energy changes in the system. To determine the spontaneity of a reaction, we need another thermodynamic quantity called *entropy*.

The Statistical Definition of Entropy

Whether a given macroscopic process is spontaneous or not depends upon what is happening at the molecular level. Consider, for example, the expansion of a gas into an evacuated bulb as depicted in Figure 8.1(a). When the stopcock is opened, gas molecules (all initially confined to bulb A) will flow spontaneously into the evacuated bulb B until the pressure of the gas is the same in both bulbs. Why does this occur? The motions of the gas molecules in bulb A are random; at any given time roughly the same number of molecules are moving in every direction. When the stopcock is opened, the molecules near the stopcock that are moving to the right will enter bulb B. As long as there are fewer molecules in bulb B, there will be more molecules moving from A to B than from B to A. This spontaneous process will continue until the pressures equalize.

Figure 8.1(b) depicts the reverse process—that is, the spontaneous movement of all the gas molecules in bulb B back into bulb A. For this to happen, all the molecules in B would have to move to the left *at the same time*. Many of the molecules are indeed moving to the left at any given time; however, because molecular motion is random, just as many molecules will be moving to the right on average. The probability that all the molecules in bulb B will move *simultaneously* to the left is vanishingly small. This process is nonspontaneous not because it is strictly impossible, but because it is so *improbable* that it would in practice never be observed. In trying to understand

A spontaneous process does not necessarily mean an instantaneous one.



A spontaneous and nonspontaneous process



When heated, HgO decomposes to give Hg and O_2 .

spontaneous processes, we must focus on the *statistical* behavior of a very large number of molecules, not on the motion of just a few of them.

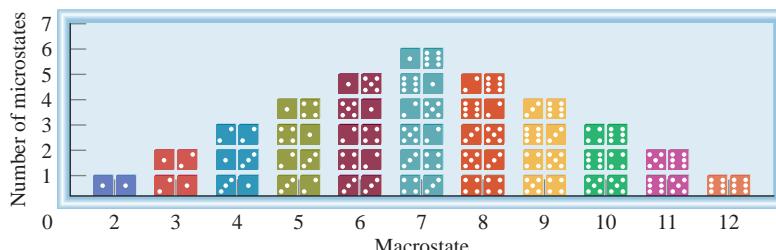
Recall from Chapter 7 that the thermodynamic state (or *macrostate*) of a system is described by relatively few variables (P , T , V , n , etc.), whereas the molecular state (or *microstate*) represents *all* the variables associated with the individual atoms or molecules that make up the system. When we completely specify the macrostate (by specifying, for example, the pressure, temperature, and volume of a sample of argon gas), there are still a very large number of distinct microstates possible. The number of microstates possible for a given macrostate can be represented by the variable W . The value of W , which determines the relative probability that a macrostate will be observed, varies widely from macrostate to macrostate. Macrostates for which W is large are more probable than those for which W is small and there are relatively few possible microstates.

The connection between the number of microstates and probability can be illustrated by rolling dice. In this analogy, we define the microstate as the numbers on each individual die and the macrostate as the sum of the numbers on all the dice thrown. If we have only one die, there are six possible outcomes given by 1, 2, 3, 4, 5, and 6. In this case, the microstates are the same as macrostates because there is only one way to achieve each total number by rolling die. If we have two dice, however, there are 36 (6×6) possible microstates, but only 11 possible macrostates (the sum of both dice) represented by the integers from 2 to 12. Therefore, at least some of the macrostates must correspond to multiple microstates. The distribution of the 36 microstates among the 11 macrostates is shown in Figure 8.2. The macrostate with the largest number of microstates, and thus the most probable corresponds to the number 7. This macrostate (7) can be achieved by six different dice combinations (microstates); that is, $W = 6$. The probability of getting 7 is equal to $1/6$, which is obtained by dividing the number of microstates that sum to 7 by the total number of possible microstates: $6/36 = 1/6$. The least probable microstates correspond to 2 and 12. For each of these macrostates there is only one microstate [(1,1) for 2 and (6,6) for 12]. For these macrostates, $W = 1$, and they each have a probability of $1/36$. The probability of rolling a 7 is much greater than rolling a 2 or 12 not because the dice are loaded—each of the 36 possible rolls are equally probable—but because there are more ways to achieve 7 than either 2 or 12.

If we increase the number of dice, the distribution in probability among the macrostates becomes much more dramatic. For example, with six dice there are 46,656 (or 6^6) possible microstates ranging from 6 to 36, for a total of 31 macrostates. For the macrostates 6 and 36 there is only one possible microstate [(1,1,1,1,1,1) and (6,6,6,6,6,6), respectively], so they both have $W = 1$ and a probability of $1/46,656$. There are, however, 4332 possible ways of rolling a 21 (the most probable macrostate) giving a probability of $4332/46,656$. Thus, we are over 4000 times more likely to roll a 21 than a 6 or 36. As we increase the number of dice, the probability of the most probable macrostate increases rapidly relative to less probable macrostates.

The symbol “ W ” comes from *Wahrscheinlichkeit*, the German word for probability.

Figure 8.2 The microstates that arise from the combination of two dice and the corresponding macrostates.



(Figure 8.3). As the number of dice approaches values corresponding to the number of molecules in a macroscopic system (Avogadro's number), the number of microstates corresponding to the most probable macrostate is so large compared to the rest that the probability of rolling anything that deviates more than very slightly from the most probable value is vanishingly small. This example shows how something that is completely random at the microstate level can generate quite predictable behavior when viewed macroscopically—just as the random motion of molecules in a gas at the molecular level gives rise to the very nonrandom ideal gas law at the macroscopic level.

For a more chemically relevant example, consider a simple system of four molecules moving rapidly between two equal compartments, as shown in Figure 8.4. There is only one way for all four molecules to be in the left compartment, four ways to have three molecules in the left compartment and one in the right compartment, and six ways to have two molecules in each of the two compartments. Thus, there are 11 possible microstates that give rise to 3 possible macrostates.¹ Of the three, macrostate III is the most probable because there are six microstates or six ways to achieve it ($W = 6$). On the other hand, macrostate I is the least probable because it has only one microstate ($W = 1$), so there is only one way to achieve it. As the number of molecules approaches macroscopic scale (Avogadro's number), the molecules will be evenly distributed between the two compartments because this macrostate has many, many more microstates than all the other macrostates.

Microstates, Entropy, and the Second Law of Thermodynamics

The probability of a particular macrostate occurring depends on the number of ways (microstates) in which the given macrostate can be achieved. If a macroscopic system

1. Actually there are still other possible ways to distribute the four molecules between the two compartments. We can have all four molecules in the right compartment (one way) or three molecules in the right compartment and one molecule in the left compartment (four ways). However, the macrostates shown in Figure 8.4 are sufficient for our discussion.

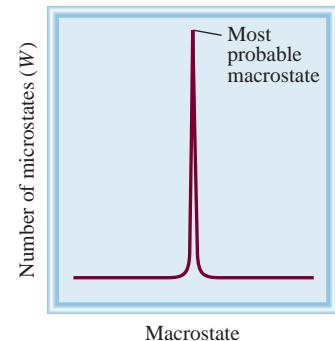
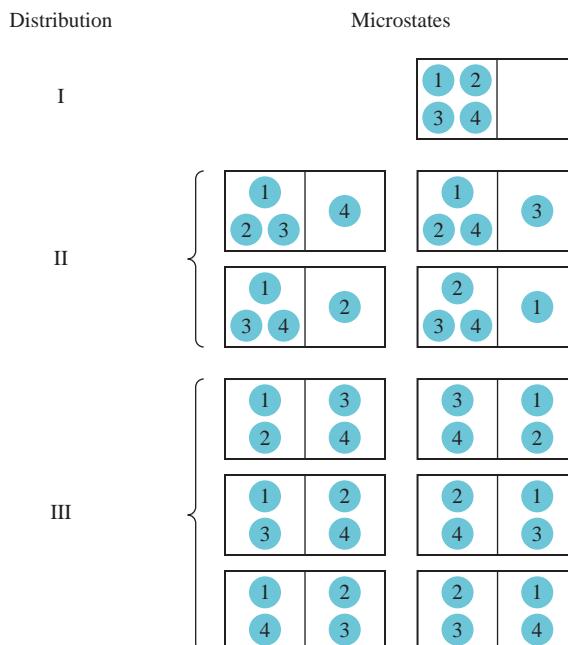


Figure 8.3 For a large number of dice, the most probable macrostate has an overwhelmingly large number of microstates compared to other macrostates.

Figure 8.4 Some possible ways of distributing four molecules between two equal compartments. Distribution I can be achieved in only one way (all four molecules in the left compartment) and has one microstate. Distribution II can be achieved in four ways and has four microstates. Distribution III can be achieved in six ways and has six microstates.

The word *entropy* was derived from the Greek work *tropē* meaning “transformation.” The prefix *en-* was added to make it similar to *energy*.



Engraved on Ludwig Boltzmann's tombstone in Vienna is his famous equation: The “log” stands for \log_e , which is the natural logarithm or \ln .

is prepared initially in a macrostate with a low probability (low W), then the system will naturally evolve to the macrostate with the highest possible probability. This process is spontaneous. The reverse process, however, in which a macrostate with high probability (large W) evolves toward one with low probability (low W) will not be observed because this process is nonspontaneous.

In thermodynamics, the spontaneity of a macroscopic process can be quantified by a thermodynamic state function called *entropy*, which is a *measure of the number of possible microstates available to a system in a given macrostate*. In 1877, Ludwig Boltzmann showed that the entropy of a system in a given macrostate is directly related to the natural log of the number of microstates (W):

$$S = k_B \ln W \quad (8.1)$$

where k_B is the Boltzmann constant ($1.380658 \times 10^{-23} \text{ J K}^{-1}$). Thus, the entropy of the system increases as the value of W increases. Like enthalpy, entropy is an extensive property.

The entropy change (ΔS) for a process in a system is

$$\Delta S = S_f - S_i \quad (8.2)$$

where S_i and S_f are the entropies of the system in the initial and final states, respectively. By combining Equations 8.1 and 8.2, we obtain

$$\Delta S = k_B \ln W_f - k_B \ln W_i$$

$$\Delta S = k_B \ln \frac{W_f}{W_i} \quad (8.3)$$

where W_i and W_f are the corresponding numbers of microstates in the initial and final macrostates, respectively. Thus, if $W_f > W_i$, then $\Delta S > 0$ and the entropy of the system increases.

The connection between entropy and the spontaneity of a process is expressed by the *second law of thermodynamics*: *The entropy of any isolated system increases in any spontaneous process and remains unchanged in an equilibrium (reversible) process*. We can consider the universe to be an isolated system; therefore, the entropy of the universe can never decrease in any spontaneous process: $\Delta S_{\text{univ}} \geq 0$, where the equality holds for a reversible process. Because the universe is made up of the system and the surroundings, the entropy change in the universe (ΔS_{univ}) for any process is the *sum* of the entropy changes in the system (ΔS_{sys}) and in the surroundings (ΔS_{surr}). Mathematically, we can express the second law of thermodynamics as follows:

$$\text{for a spontaneous process: } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \quad (8.4)$$

$$\text{for a reversible (or equilibrium) process: } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \quad (8.5)$$

For a spontaneous process, ΔS_{univ} must be greater than zero, but there are no restrictions on either ΔS_{sys} or ΔS_{surr} . Thus, either ΔS_{sys} or ΔS_{surr} can be negative, as long as the sum of these two quantities is greater than zero. For an equilibrium process, ΔS_{univ} is zero. In this case, ΔS_{sys} and ΔS_{surr} must be equal in magnitude, but opposite in sign. If ΔS_{univ} is negative, then the process is nonspontaneous in the direction described. Instead, it is spontaneous in the *opposite* direction.

Example 8.1

Calculate the entropy change for the process (in J K^{-1}) depicted in Figure 8.1(a) where initially there is 1.000 mole of gas in the left bulb. Assume that the gas behaves ideally and that the process is isothermal.

Strategy Use Equation 8.3 to calculate the entropy change. To do so, we need to determine the ratio W_f/W_i for the process in Figure 8.1(a).

Solution For a general process, determining ΔS using Equation 8.3 is complicated; however, the properties of ideal gases greatly simplify the matter. First, because the process is isothermal, the temperature of the gas does not change. From the kinetic theory of gases (Section 5.4), constant temperature implies that there is no change in the velocity distribution of the gas molecules. Thus, only the properties of the microstates involving position can change as we go from the initial state to the final state.

Suppose, for example, that there is only one gas particle present in the system. Because the two bulbs have equal volumes, the particle has twice as many position microstates available in the final state as in the initial state: $W_f/W_i = 2$. If two particles are present to start with, then $W_f/W_i = (2 \times 2)/1 = 4/1 = 4$ because each of the two particles in the final state can be independently either in the left bulb or the right bulb ($2 \times 2 = 4$ total possibilities), but in the initial state both particles are constrained to be in the left bulb (1 possibility). If we have N particles in the system, the ratio of microstates becomes

$$\frac{W_f}{W_i} = 2 \times 2 \times 2 \dots = 2^N$$

We can now apply Equation 8.3:

$$\begin{aligned}\Delta S &= k_B \ln \frac{W_f}{W_i} \\ &= k_B \ln 2^N \\ &= Nk_B \ln 2\end{aligned}$$

where we have used the fact that $\ln a^b = b \ln a$. Recall from Section 5.4 that the Boltzmann constant is related to the gas constant by $k_B = R/N_A$, so the entropy change becomes

$$\begin{aligned}\Delta S &= \frac{N}{N_A} R \ln 2 \\ &= nR \ln 2\end{aligned}$$

where $n = N/N_A$ is the number of moles of gas present. So for 1.000 mol of gas we have

$$\begin{aligned}\Delta S &= (1.000 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln 2 \\ &= 5.763 \text{ J K}^{-1}\end{aligned}$$

Check The process depicted in Figure 8.1(a) is spontaneous, so the entropy change should be positive (according to the second law of thermodynamics), which our calculation confirms.

Comment Example 8.1 shows why entropy is a more convenient way to describe the process than W . For 1 mole of particles, the ratio of the number of microstates in the

—Continued

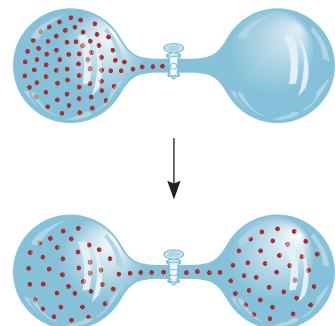


Figure 8.1 (a)

Continued—

final and initial states is $2^{N_A} = 2^{6.02 \times 10^{23}} \approx 10^{1.8 \times 10^{23}}$, which is a very large number indeed!

Practice Exercise Repeat the calculation in Example 8.1 except assume the volume of the right-hand bulb in Figure 8.1(a) has twice the volume of the left-hand bulb.

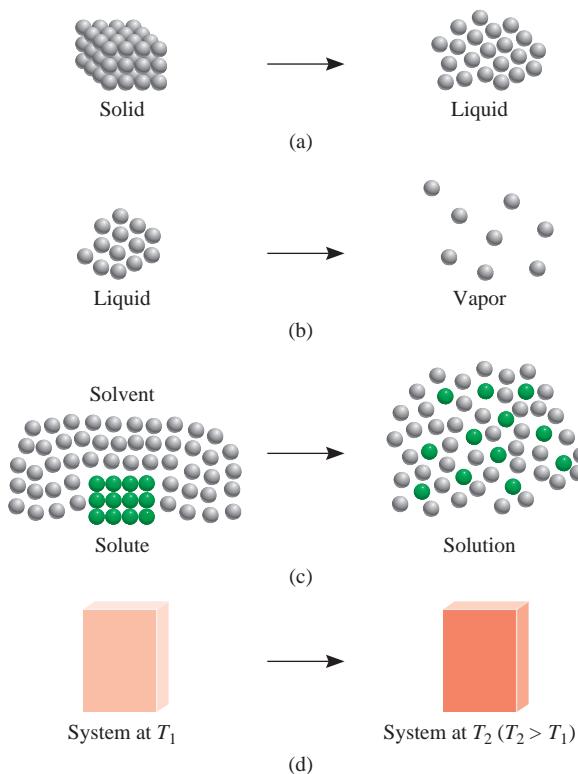
The Physical Interpretation of Entropy

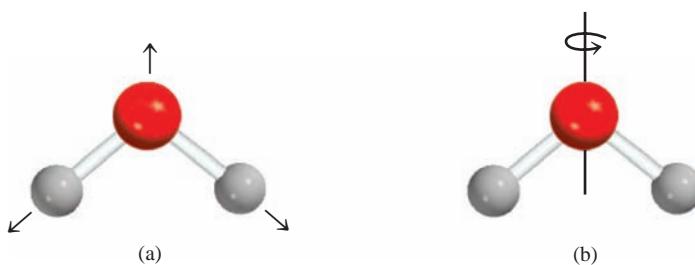
Entropy is often described as a measure of disorder or randomness. These terms should be used with a great deal of caution, however, because they are subjective and can lead to erroneous conclusions.² It is preferable, instead, to view the change in entropy of a system in terms of the change in the number of microstates of the system.

Consider the situations shown in Figure 8.5. In the solid in Figure 8.5(a), the atoms or molecules are held relatively rigidly in the crystal lattice. In the liquid, though, these atoms or molecules can occupy many more positions as they move away from the lattice points. Also, for most materials (water is an exception), the liquid phase is less dense than the solid phase, so molecules in a liquid have a greater available volume in which to move. Consequently, the number of microstates increases when a solid transitions into a liquid because there are now many more ways to arrange the particles. Therefore, the solid-to-liquid phase transition should result in

2. See, for example, B. Laird, "Entropy, Disorder and the Freezing Transition," *Journal of Chemical Education*, **76**, 255 (1998).

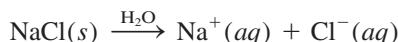
Figure 8.5 Processes that lead to an increase in entropy of the system: (a) melting: $S_{\text{liquid}} > S_{\text{solid}}$, (b) vaporization: $S_{\text{vapor}} > S_{\text{liquid}}$, (c) dissolving, and (d) heating: $S_{T_2} > S_{T_1}$ (if $T_2 > T_1$).





an increase in entropy because the number of microstates has increased. Similarly, the vaporization process [Figure 8.5(b)] should also lead to an increase in the entropy of the system. The increase will be considerably greater than that for melting, however, largely because the change in available volume in going from liquid to vapor is much greater than that corresponding to a solid-liquid transition.

The solution process [Figure 8.5(c)] usually leads to an increase in entropy, too. When a sugar crystal (a nonelectrolyte) dissolves in water, the highly ordered structure of the solid and part of the ordered structure of water break down. Thus, the solution has a greater number of microstates than the pure solute and pure solvent combined. When an ionic solid (an electrolyte) such as NaCl dissolves in water, two factors contribute to an increase in entropy: the solution process (the mixing of the solute with solvent) and the dissociation of the compound into ions:



More particles lead to a greater number of microstates. Hydration, however, causes water molecules to become more structured around the ions. This process decreases entropy because it reduces the number of microstates available to the solvent molecules. For small, highly charged ions such as Al^{3+} and Fe^{3+} , the decrease in entropy due to hydration can exceed the increase in entropy due to mixing and dissociation, so the entropy change for the overall process can actually be negative.

Heating also increases the entropy of a system [Figure 8.5(d)]. In addition to translational motion (that is, the motion through space of the whole molecule), molecules can also rotate and vibrate (Figure 8.6). As the temperature increases, the energies associated with all types of molecular motion increase. This increase in energy is distributed or dispersed among the quantized energy levels. Consequently, more microstates become available at higher temperatures, which means the entropy of the system increases with increasing temperature.

Example 8.2

Predict whether the entropy change is greater or less than zero for each of the following processes: (a) freezing ethanol, (b) evaporating a beaker of liquid bromine at room temperature, (c) dissolving glucose in water, and (d) cooling nitrogen gas from 80°C to 20°C.

Strategy To determine the direction of the entropy change in each case, we must decide whether the number of microstates of the system increases or decreases. The sign of ΔS will be positive if the number of microstates increases and negative if the number decreases.

—Continued

Figure 8.6 (a) A vibrational motion in a water molecule. The atoms are displaced, as shown by the arrows, and then reverse their directions to complete a cycle of vibration. (The vibration shown is one of three possible vibrational modes of water.) (b) A rotational motion of a water molecule about an axis through the oxygen atom. The molecule can also rotate with respect to the other two mutually perpendicular axes.



Bromine is a fuming liquid at room temperature.

Continued—

Solution (a) Upon freezing, the ethanol molecules are held rigid in position. This phase transition reduces the number of microstates and therefore the entropy decreases, that is, $\Delta S < 0$.

(b) Evaporating bromine increases the number of microstates because the Br_2 molecules can occupy many more positions in nearly empty space. Therefore, $\Delta S > 0$.

(c) Glucose is a nonelectrolyte (that is, it does not disassociate into ions in aqueous solution). The solution process disperses the glucose molecules among the water molecules, so we expect $\Delta S > 0$.

(d) The cooling process decreases various molecular motions. This leads to a decrease in microstates, and so $\Delta S < 0$.

Practice Exercise How does the entropy of a system change for each of the following processes: (a) condensing water vapor, (b) forming sucrose crystals from a supersaturated solution, (c) heating hydrogen gas from 60°C to 80°C, and (d) subliming dry ice?

8.2 | The Entropy Change for a Process Can Be Calculated Using the Thermodynamic Definition of Entropy

Equation 8.1 is a statistical definition of entropy. Defining entropy in terms of probability provides a molecular interpretation of entropy changes as well as allowing for the calculation of entropy changes in simple systems, such as that of an ideal gas. In general, though, Equation 8.1 is not used to determine entropy changes in complex systems, such as those in which chemical reactions occur, because the calculation of W is too difficult. Fortunately, in addition to the statistical definition, there is a thermodynamic definition of entropy that allows us to determine entropy changes from changes in experimentally measurable thermodynamic quantities, such as heat, energy, and enthalpy.

The Thermodynamic Definition of Entropy

In 1865, building on the work of Kelvin, Sadi Carnot,³ and others who studied the efficiency of heat engines, Rudolf Clausius⁴ postulated that the entropy change of a system undergoing an infinitesimal reversible process was the heat absorbed (dq_{rev}) divided by the absolute temperature T (in kelvins) of the system:

$$dS = \frac{dq_{\text{rev}}}{T} \quad (8.6)$$

Thus, the entropy change for any process between two states A and B can be calculated by integrating Equation 8.6 to give

$$\Delta S = \int_{\text{state A}}^{\text{state B}} \frac{dq_{\text{rev}}}{T} \quad (8.7)$$

3. Nicolas Léonard Sadi Carnot (1796–1832). French physicist. Son of a famous French general, Carnot was a pioneer in the study of the relationship between heat and mechanical work.

4. Rudolf Julius Emanuel Clausius (1822–1888). German physicist. The work of Clausius was mainly in electricity, the kinetic theory of gases, and thermodynamics.

If the process takes place at constant temperature, Equation 8.7 can be integrated to give

$$\Delta S = \frac{q_{\text{rev}}}{T} \quad \text{constant temperature} \quad (8.8)$$

Clausius's analysis showed that, although q_{rev} is not a state function and is path dependent, the entropy changes calculated using Equation 8.7 are independent of the path taken, so entropy is a state function.

We saw in Section 7.1 that the work done by a system ($-w$) is maximum if the process is reversible, that is, $-w \leq -w_{\text{rev}}$. Therefore, because $\Delta U = q + w$ is independent of the nature of the process (U is a state function), the heat absorbed during a process is always less than or equal to that absorbed reversibly: $q \leq q_{\text{rev}}$. Combining this with Equation 8.6 gives

$$dS \geq \frac{dq}{T} \quad (8.9)$$

where the equality holds if the process is reversible. Equation 8.9 is known as the **Clausius inequality**. If the system is isolated then $dq = 0$ and Equation 8.9 yields $dS \geq 0$ in accordance with our earlier statement of the second law of thermodynamics.

In general, the thermodynamic definition of entropy (Equations 8.6 to 8.8) yields the same value for the entropy change of a process as Boltzmann's statistical definition (Equation 8.3) for the same process. Consider, for example, the entropy change in the reversible and isothermal (constant temperature) expansion of n moles of an ideal gas from an initial volume V_1 to a final volume V_2 . We saw in Section 7.1 that the heat absorbed by the gas in such a reversible process is given by (Equation 7.8)

$$q_{\text{rev}} = nRT \ln \frac{V_2}{V_1}$$

Because this process is isothermal, we can use Equation 8.8 to calculate the thermodynamic entropy change

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{nRT \ln(V_2/V_1)}{T}$$

$$\Delta S = nR \ln \frac{V_2}{V_1} \quad \text{for an ideal gas} \quad (8.10)$$

Although we began our discussion of entropy with the statistical view, the thermodynamic view was developed first.

If $V_2 = 2V_1$, as in the process depicted in Figure 8.1, then we have

$$\Delta S = nR \ln \frac{2V_1}{V_1} = nR \ln 2$$

This is exactly the same value that we obtained for this process in Example 8.1 using the statistical definition of entropy.

Equation 8.9 can also be written in terms of pressure changes. For an ideal gas at a fixed temperature, Boyle's law (Equation 5.11) states that $V_2/V_1 = P_1/P_2$, so Equation 8.10 becomes

$$\Delta S = nR \ln \frac{P_1}{P_2} \quad \text{for an ideal gas} \quad (8.11)$$

Example 8.3

At a constant temperature of 300 K, 1.00 mole of argon gas is expanded from an initial volume of 20.0 L to a final volume of 50.0 L. Assuming ideal behavior, calculate the entropy change of the gas for this process.

Strategy Because entropy is a state function, changes in entropy are independent of the path taken; therefore, we can assume that the expansion occurs reversibly for the purposes of calculating ΔS , allowing us to use Equation 8.9.

Solution Plugging the values of n , R , V_1 (V_{initial}), and V_2 (V_{final}) into Equation 8.9, we obtain the following value for ΔS :

$$\begin{aligned}\Delta S &= (1.00 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln \frac{50.0 \text{ L}}{20.0 \text{ L}} \\ &= 7.62 \text{ J K}^{-1}\end{aligned}$$

Check The expansion of a gas is a spontaneous process, so we expect that the entropy change should be positive. Our result here is consistent with that fact.

Practice Exercise Calculate the entropy change for 50.0 g of N₂ gas that is compressed at a constant temperature of 50°C from an initial pressure of 1.00 bar to a final pressure of 3.00 bar. Assume ideal behavior.

The typical magnitudes of entropy changes in chemistry are such that they are generally reported in $\text{J mol}^{-1} \text{ K}^{-1}$ instead of $\text{kJ mol}^{-1} \text{ K}^{-1}$.

Entropy Change Due to Heating

We learned at the end of Section 8.1 [recall Figure 8.5(d)] that the entropy of a system increases when the temperature of the system is raised from T_1 to T_2 . Using the thermodynamic definition of entropy, we can calculate the change in entropy for a system upon heating (or cooling). Beginning with Equation 8.6,

$$dS = \frac{dq_{\text{rev}}}{T}$$

then integrating this equation from an initial state with temperature T_1 to a final temperature T_2 gives

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T} \quad (8.12)$$

As discussed in Section 7.3, the amount of heat added in the course of a temperature change can be determined from the heat capacity C using the differential version of Equation 7.16:

$$dq = C dT \quad (8.13)$$

Combining Equations 8.12 and 8.13 gives

$$\Delta S = \int_{T_1}^{T_2} \frac{C}{T} dT \quad (8.14)$$

The value of C to use in Equation 8.14 depends upon the nature of the specific process under consideration. If the process occurs at constant volume, then the constant-volume heat capacity C_V should be used, giving

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T} dT \quad (\text{constant } V) \quad (8.15)$$

Similarly, the constant-pressure heat capacity C_P should be used for a constant pressure process, giving

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT \quad (\text{constant } P) \quad (8.16)$$

If the temperature range is small, we can assume that the heat capacity (C_P or C_V) is independent of temperature, giving (after integration)

$$\Delta S = C_V \ln \frac{T_2}{T_1} \quad (\text{constant } V, T_2 - T_1 \text{ small}) \quad (8.17)$$

and

$$\Delta S = C_P \ln \frac{T_2}{T_1} \quad (\text{constant } P, T_2 - T_1 \text{ small}) \quad (8.18)$$

Example 8.4

Calculate the increase in entropy when 250 g of water is heated at constant pressure from 20°C to 50°C. The molar heat capacity of water at constant pressure is 75.3 J K⁻¹ mol⁻¹. Assume that C_P is constant over this temperature range.

Strategy Use Equation 8.18 to solve this problem, but remember that the total heat capacity of the water (or any material) is its molar heat capacity multiplied by the number of moles of substance. Also, we must convert all Celsius temperatures to absolute temperatures (kelvins).

Solution We are given the molar heat capacity of water (\bar{C}_P), not the heat capacity (C_P), so we must determine the number of moles of water (n) that are being heated and use $n\bar{C}_P$ in Equation 8.18 instead of C_P .

$$n_{\text{water}} = \frac{250 \text{ g}}{18.02 \text{ g mol}^{-1}} = 13.9 \text{ mol}$$

From Equation 8.18, we have

$$\begin{aligned} \Delta S &= C_P \ln \frac{T_2}{T_1} = n\bar{C}_P \ln \frac{T_2}{T_1} \\ &= (13.9 \text{ mol})(75.3 \text{ J mol}^{-1} \text{ K}^{-1}) \ln \frac{323.15 \text{ K}}{293.15 \text{ K}} = 1.02 \times 10^2 \text{ J K}^{-1} \end{aligned}$$

Practice Exercise Calculate the entropy change that arises when a 30.0-L sample of argon gas, initially at a pressure of 1.00 bar and a temperature of 300 K, is heated at constant volume to a final temperature of 400 K. Assume ideal gas behavior.

Entropy Change Due to a Phase Transition

When a solid melts at its equilibrium melting temperature, the system absorbs heat reversibly, because the solid and liquid are in equilibrium under these conditions. During the melting process, both temperature and pressure remain fixed. Because this is a constant-pressure process, the heat absorbed by the system can be equated to the enthalpy of fusion, ΔH_{fus} (see Section 6.6), that is, $q_{\text{rev}} = \Delta H_{\text{fus}}$. Because this process is isothermal, the entropy of fusion ΔS_{fus} can be obtained using Equation 8.8:

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_m} \quad (8.19)$$

where T_m is the melting temperature (for example, 273.15 K for ice at 1 atm). Using a similar analysis for the boiling process, the entropy of vaporization ΔS_{vap} is

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b} \quad (8.20)$$

where ΔH_{vap} is the enthalpy of vaporization and T_b is the boiling temperature (for example, 373.15 K for water at 1 atm). A similar formula holds for sublimation.

Example 8.5

Calculate the molar entropies of fusion and vaporization for water at its normal melting point and boiling point. The molar enthalpies of vaporization and fusion of water are given in Tables 7.7 and 7.8, respectively.

Strategy Use Equation 8.19 to calculate the entropy change for fusion and Equation 8.20 to calculate the entropy change for vaporization. From Tables 7.7 and 7.8, we find $\Delta H_{\text{vap}} = 40.79 \text{ kJ mol}^{-1}$ and $\Delta H_{\text{fus}} = 6.01 \text{ kJ mol}^{-1}$, for water at its normal boiling and melting points, respectively.

Solution Using Equation 8.19, we have for the entropy of fusion

$$\begin{aligned}\Delta S_{\text{fus}} &= \frac{\Delta H_{\text{fus}}}{T_m} = \frac{6.01 \text{ kJ mol}^{-1}}{273.15 \text{ K}} \\ &= 0.0220 \text{ kJ K}^{-1} \text{ mol}^{-1} = 22.0 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Similarly, using Equation 8.20, we have for the entropy of vaporization

$$\begin{aligned}\Delta S_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_b} = \frac{40.79 \text{ kJ mol}^{-1}}{373.15 \text{ K}} \\ &= 0.1094 \text{ kJ K}^{-1} \text{ mol}^{-1} = 109.4 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Practice Exercise Calculate the entropy change when 1.00 mol of dry ice (solid CO_2) sublimes at the equilibrium sublimation temperature of -78.5°C . The enthalpy of sublimation for CO_2 is 26.2 kJ mol^{-1} .

Table 8.1

The Normal Boiling Point (T_b), Molar Enthalpies of Vaporization, (ΔH_{vap}) and Molar Entropy of Vaporization (ΔS_{vap}) of Several Substances.

| Substance | T_b (K) | ΔH_{vap} (kJ mol $^{-1}$) | ΔS_{vap} (J mol $^{-1}$ K $^{-1}$) |
|---------------------------------------|-----------|---|--|
| Carbon tetrachloride (CCl $_4$) | 349.8 | 32.5 | 92.9 |
| Ethanol (C $_2$ H $_5$ OH) | 351.4 | 39.3 | 111.8 |
| Diethyl ether (C $_2$ H $_5$) $_2$ O | 308.6 | 27.4 | 88.8 |
| Benzene (C $_6$ H $_6$) | 353.4 | 31.0 | 87.7 |
| Mercury (Hg) | 630 | 59.0 | 93.7 |
| Methane (CH $_4$) | 109 | 9.2 | 84 |
| Water (H $_2$ O) | 373.15 | 40.79 | 109.4 |

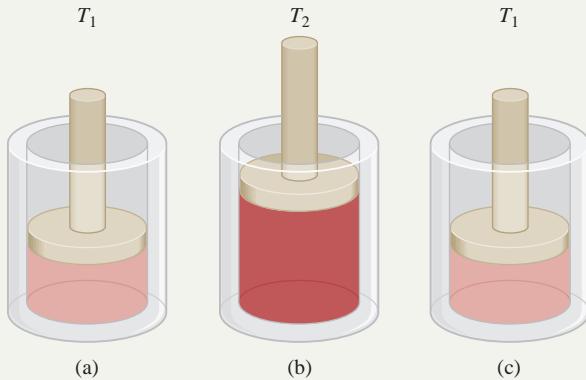
As illustrated by the calculation in Example 8.5, ΔS_{vap} is usually greater than ΔS_{fus} for the same substance. As we saw in Chapter 6, both solids and liquids are dense phases and possess a significant amount of structure—illustrated by the crystal structure for a solid (Section 6.3) and the radial distribution function of the liquid (Section 6.1). In contrast, a gas phase is unstructured and very low density, which allows for a great deal of freedom of motion. As a consequence, the change in the number of microstates corresponding to solid-liquid transition microstates is less than the corresponding change associated with the liquid-to-vapor transition, and the entropy of vaporization (and of sublimation) will be considerably larger than the entropy of fusion.

The molar entropies of vaporization of a number of liquids are listed in Table 8.1. In the late nineteenth century, Frederick Trouton⁵ observed that the molar entropy of vaporization of different liquids had quite similar values and averaged about 88 J mol $^{-1}$ K $^{-1}$. This observation is known as *Trouton's rule* and provides a convenient empirical “rule-of-thumb” for estimating vaporization entropies. On a molecular level, we can understand Trouton's rule as implying that the molecular-level structures of most liquids are similar, as are the structures of their corresponding vapor phases. Therefore, the increase in the number of available microstates upon vaporization will be roughly the same for most substances, implying similar ΔS_{vap} values. In Table 8.1, water and ethanol have ΔS_{vap} values that are significantly higher than those predicted by Trouton's rule. These two liquids possess significant hydrogen bonding leading to a substantially more ordered local structure than present in non-hydrogen-bonded liquids. As a result, the liquid phases of water and ethanol have a smaller number of available microstates than is typical for other liquids. The structures of water and ethanol in the gas phase, however, are similar to other liquids because the molecules are so far apart that hydrogen bonding is negligible. Therefore, hydrogen-bonded liquids will exhibit a larger than typical change in the number of available microstates and a correspondingly larger value of ΔS_{vap} .

5. Frederick Thomas Trouton (1863–1922). Irish experimental physicist. Trouton was elected Fellow of the Royal Society in 1897 and served as the Quain Professor of Physics at University College London from 1902–1914.

The Efficiency of Heat Engines: The Carnot Cycle

An engine is a machine that converts energy to work; a *heat engine* is a machine that converts *thermal energy* to work. Heat engines play an essential role in our technological society, ranging from automobile engines to the giant steam turbines that run generators to produce electricity. Regardless of the type of heat engine, its efficiency level, the amount of useful work that we can get out of the engine for a given amount of heat input, is governed by the second law of thermodynamics.

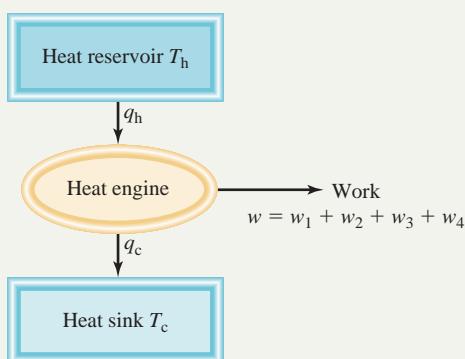


A simple heat engine. (a) The engine is initially at T_1 . (b) When heated to T_2 , the piston is pushed up due to gas expansion. (c) When cooled to T_1 , the piston returns to its original position.

The figure shows a simple form of a heat engine. A cylinder fitted with a weightless piston is initially at a temperature T_1 . The cylinder is then heated to a higher temperature T_2 . The gas in the cylinder expands and pushes up the piston. When the cylinder is subsequently cooled back down to T_1 , the apparatus returns to its original state. By repeating this cycle, the up-and-down movement of the piston can be made to do mechanical work.

A unique feature of heat engines is that some heat must be given off to the surroundings when they do work. With the piston in the up position, no further work can be done if we do not cool the cylinder back to T_1 . The cooling process removes some of the thermal energy that could otherwise be converted to work and thereby limits the efficiency of heat engines.

We can use the second law of thermodynamics to establish precise theoretical limits on the efficiency of heat engines.



A schematic diagram of a Carnot heat engine

To do this, we must consider an idealized model of a heat engine called a *Carnot heat engine*, which operates between a high-temperature heat source at temperature T_h and a colder heat sink at temperature T_c , as shown.

A Carnot heat engine operates according to the following four-step cycle:

Step 1 The engine absorbs an amount of heat q_h from the high-temperature heat source at a constant temperature of T_h while delivering an amount of work w_1 . For this step $q = q_h$ and $w = -w_1$ (the negative sign is necessary because work is being done by the system, not on the system).

Step 2 The engine is decoupled from the high-temperature heat source and delivers an amount of work w_2 . Because the engine is not coupled to a heat source/sink in this step, no heat is transferred and the process is adiabatic. The loss of energy due to work without a corresponding heat input causes the temperature of the engine to drop to T_c . In this step, $q = 0$ and $w = -w_2$.

Step 3 The engine is coupled to the low-temperature heat sink and delivers an amount of heat energy q_c to the heat sink, while simultaneously delivering an amount of work w_3 . For this step, $q = -q_c$ (heat is transferred out of the system) and $w = -w_3$.

Step 4 The engine is decoupled from the low-temperature heat sink and delivers an amount of work w_4 . As in step 3, this process is adiabatic. The energy gained by the engine due to work without a corresponding heat input causes the temperature of the engine to return to T_h , completing the cycle. In this step, $q = 0$ and $w = -w_4$. (Again the negative sign is necessary because we are defining w_4 as the work delivered, not the work done on the system. Actually, in this case w_4 is negative and w is positive, that is, work is being done on the system by the surroundings.)

Because this is a cyclic process, the total change in any state function of the system (the heat engine) must be zero—that is, $\Delta U_{\text{sys}}(\text{cycle}) = 0$ and $\Delta S_{\text{sys}}(\text{cycle}) = 0$.

From the first law of thermodynamics, we have

$$\begin{aligned}\Delta U_{\text{sys}}(\text{cycle}) &= (q + w)_{\text{Step 1}} + (q + w)_{\text{Step 2}} \\ &\quad + (q + w)_{\text{Step 3}} + (q + w)_{\text{Step 4}} \\ &= (q_h - w_1) + (0 - w_2) \\ &\quad + (-q_c - w_3) + (0 - w_4) \\ &= q_h - q_c - (w_1 + w_2 + w_3 + w_4) \\ &= q_h - q_c - w_{\text{delivered}}\end{aligned}$$

where we have defined $w_{\text{delivered}}$ as the total amount of work delivered in the four steps of the cycle. Because $\Delta U_{\text{cycle}} = 0$, we have

$$q_h - q_c - w_{\text{delivered}} = 0$$

giving

$$w_{\text{delivered}} = q_h - q_c \quad (1)$$

In the operation of the Carnot heat engine, a given amount of energy is extracted from the high-temperature heat source. Some of this energy is converted into work, and some is lost to the low-temperature heat sink. We can define the efficiency (ε) of a heat engine as the ratio of the work output ($w_{\text{delivered}}$) to the heat input (q_h):

$$\begin{aligned}\varepsilon &= \frac{\text{net work done by heat engine}}{\text{heat absorbed by engine}} \\ &= \frac{w_{\text{delivered}}}{q_h}\end{aligned}$$

Using Equation (1) above we have

$$\varepsilon = \frac{q_h - q_c}{q_h}$$

giving

$$\varepsilon = 1 - \frac{q_c}{q_h} \quad (2)$$

Thus, based on first-law considerations, the efficiency of a heat engine is reduced according to the amount of heat energy transferred to the low temperature heat sink. However, nothing in the first law prevents q_c from being zero giving an efficiency of 1 (or 100 percent efficiency). To understand the restrictions on the efficiency of a heat engine, we must turn to the second law.

According to the second law (Equations 8.4 and 8.5), the total entropy change of the system plus surroundings must be greater than or equal to zero:

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

where the equal sign applies if the engine is operating reversibly. Because steps 1 through 4 of the Carnot heat engine operation represent a cyclic process, $\Delta S_{\text{sys}} = 0$, giving

$$\Delta S_{\text{surr}}(\text{cycle}) \geq 0 \quad (3)$$

Furthermore, if we assume that the heat source, heat sink, and work sink are much larger than the system, then energy transfer to these external bodies can be assumed to take place reversibly, and the entropy changes can be calculated using Equation 8.8 ($\Delta S = q_{\text{rev}}/T$); Equation (3) then becomes

$$\Delta S_{\text{surr}}(\text{cycle}) = -\frac{q_h}{T_h} + \frac{q_c}{T_c} \geq 0$$

which, after some rearrangement, gives

$$\frac{q_c}{q_h} \geq \frac{T_c}{T_h}$$

Substitution of this inequality into Equation (2) above yields

$$\varepsilon \leq 1 - \frac{T_c}{T_h} \quad (4)$$

Thus, the thermodynamic efficiency of the Carnot heat engine is at a maximum when the engine is operating reversibly and can never be 1, or 100 percent, because T_c can never be zero and T_h cannot be infinite. In other words, we can never convert heat totally into work; some of it escapes into the surroundings as waste heat.

Although we have derived the thermodynamic efficiency inequality [Equation (4) above] specifically for the Carnot heat engine, it can be shown that no heat engine operating between a hot and a cold heat source or sink can be more efficient than the Carnot engine when operating reversibly. In addition, all such heat engines when operating reversibly have the same efficiency as the Carnot engine.

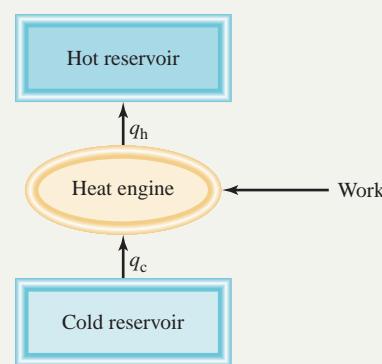
If we do work *on* a heat engine instead of extracting work, it is possible to remove heat from a low temperature heat source and deposit it in a high temperature heat sink, against the natural tendency for heat to flow from hot to cold bodies. Two familiar devices that reverse the direction of heat flow are refrigerators and air conditioners. We can model such devices using a Carnot engine operating in reverse (see the figure). The performance of a refrigerator or air conditioner is measured by the *coefficient of performance* (COP), which is the ratio of the heat extracted from the cold heat source to the amount of work applied:

$$\text{COP} = \frac{q_c}{w_{\text{done}}}$$

Using an analysis similar to that used to determine the efficiency of a Carnot heat engine, the maximum COP of a refrigerator or air conditioner is given by

$$\text{COP} \leq \frac{T_c}{T_h - T_c} \quad (5)$$

Consider, for example, a refrigerator set at 273 K in a room with an ambient temperature of 293 K. Equation (5) above yields a COP of about 14. In reality, the COP values of commercially available refrigerators are in the range of only two to six because these devices do not operate under optimal reversible conditions.



A Carnot engine working in the reverse direction. Refrigerators and air conditioners supply work to remove heat q_c from a cold heat source and deposit heat q_h into a hot heat sink.

8.3 | The Third Law of Thermodynamics Allows Us to Determine Absolute Entropies

We cannot measure the absolute internal energy U or enthalpy H because the zero of energy is arbitrary. As a result, we are usually only interested in determining changes in these properties (ΔU and ΔH) during a process. However, it is possible to determine the absolute entropy of a substance. This is because of the *third law of thermodynamics*, which states that *the entropy of a pure substance in its thermodynamically most stable form is zero at the absolute zero of temperature, independent of pressure*. For the vast majority of substances, the thermodynamically most stable form at 0 K is a perfect crystal. An important exception is helium, which remains liquid, due to its large quantum zero-point motion, at 0 K for pressures below about 10 bar.

The third law is a consequence of the statistical nature of entropy as reflected in Boltzmann's formula (Equation 8.1), which relates the entropy to W , the number of molecular quantum states (microstates) consistent with the macroscopic conditions. At $T = 0$, there is no available thermal energy, and the thermodynamically most stable state is the lowest possible energy state (the ground state). In general, this state is unique, so $W = 1$ for a system at 0 K. From Boltzmann's formula we then have

$$S(T = 0 \text{ K}) = k_B \ln W = k_B \ln (1) = 0$$

We can never reach absolute zero, however (although we can get very, very close), so we can state the third law mathematically as

$$\lim_{T \rightarrow 0 \text{ K}} S = 0$$

for a pure substance in its thermodynamically most stable state.

At temperatures above absolute zero, the entropy will be greater than zero due to thermal motion—even for perfect crystals. If the material is impure or if it has defects, then its entropy will be greater than zero, even at 0 K. The significance of the third law is that it enables us to calculate the absolute value of the entropy of a substance.

Third Law or Absolute Entropies

If we heat a system at constant pressure P from an initial temperature T_1 to a final temperature T , the entropy at T can be related to that at T_1 using Equation 8.16, assuming that no phase transitions intervene:

$$S(T) = S(T_1) + \int_{T_1}^T \frac{C_P}{T} dT$$

If we take $T_1 = 0$ K, then we have

$$S(T) = \int_0^T \frac{C_P}{T} dT \quad (8.21)$$

because $S(T = 0 \text{ K})$ is zero. Equation 8.21 defines the absolute entropy S of the substance at the pressure P . If the interval $T = 0 \text{ K}$ to T contains a phase transition at a temperature T_{trans} , then we add $\Delta S = \Delta H_{\text{trans}}/T_{\text{trans}}$ to the entropy calculated in Equation 8.21 to account for the entropy change due to the phase transition. Because C_P and ΔH_{trans} are measurable quantities, this procedure makes it possible to experimentally determine S for any substance. Figure 8.7 shows a typical graph of the increase in S with temperature from absolute zero to a temperature above the boiling temperature, noting the contributions of the melting and boiling transitions.

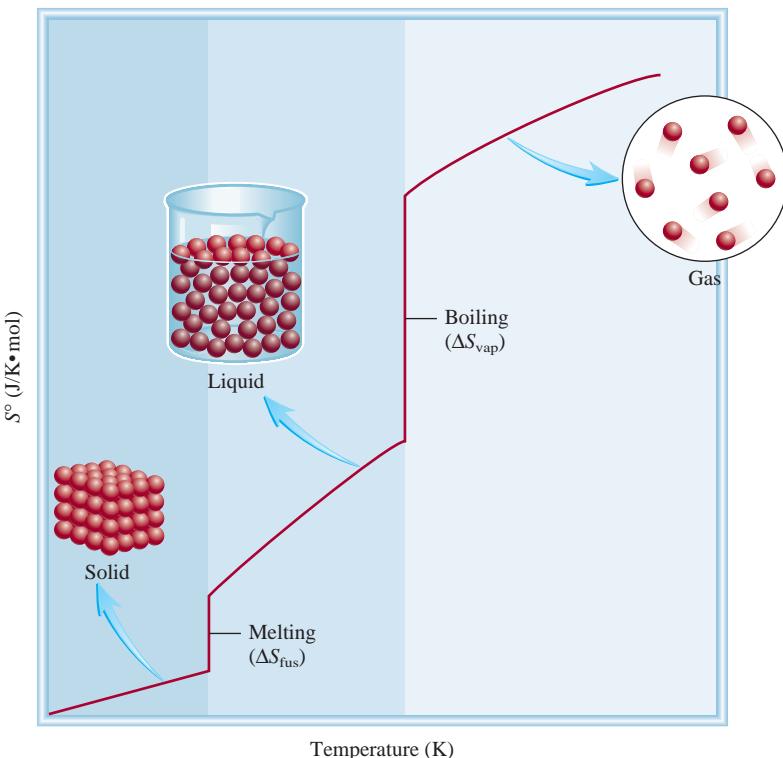


Figure 8.7 The increase in the entropy of a substance at constant pressure from absolute zero to its gaseous state at some temperature. The vertical jumps at the melting and boiling points represent the contributions to S due to the solid-liquid and liquid-vapor phase transitions.

Entropies calculated using Equation 8.21 (with phase transitions) are called **third-law** (or) **entropies** because these values are not measured relative to some reference state. Third-law entropies per mole of material measured at the standard pressure of 1 bar are referred to as **standard molar entropies**, denoted by S° . Table 8.2 lists standard molar entropies for a variety of inorganic and organic substances—values for many other substances are given in Appendix 2. The units of S° are $\text{J mol}^{-1} \text{K}^{-1}$, in contrast to ΔH_f° values, which are generally given in kJ mol^{-1} . Entropies of elements and compounds are all positive (that is, $S^\circ > 0$) for all $T > 0 \text{ K}$. By contrast, the standard enthalpy of formation (ΔH_f°) for elements in their stable form is arbitrarily set equal to zero, and for compounds it may be positive or negative.

According to Table 8.2, the standard entropy of water vapor is greater than that of liquid water. Similarly, bromine vapor has a higher standard entropy than liquid bromine, and iodine vapor has a greater standard entropy than solid iodine. For different substances in the same phase, molecular complexity determines which ones have higher entropies. Both diamond and graphite are solids, but diamond has a more regular structure⁶ and hence a smaller number of microstates (see Figure 6.27). Therefore, diamond has a smaller standard entropy than graphite. Ethane (C_2H_6 , a component of natural gas) has a more complex structure than methane (CH_4 , also a component of natural gas), and hence ethane has more ways to execute molecular motions, which also increases its number of microstates. Ethane, therefore, has a

6. Although both are crystalline, diamond and graphite have quite different structures. Diamond is a crystalline solid with a three-dimensional tetrahedral network of bonds. The structure of graphite consists of sheets of carbon atoms arranged in a two-dimensional network of hexagons. The interaction between these graphite sheets is relatively weak, which gives graphite both its lubricating property and a higher entropy than that of the more rigidly packed diamond.

Table 8.2 Standard Molar Entropies at 298.15 K and 1 Bar for Select Inorganic and Organic Substances.

| Substance | $S^\circ \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$ | Substance | $S^\circ \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$ |
|---------------------------|--|--|--|
| $\text{He}(g)$ | 126.15 | $\text{N}_2\text{O}(g)$ | 219.99 |
| $\text{Ne}(g)$ | 146.33 | $\text{O}_2(g)$ | 205.0 |
| $\text{Ar}(g)$ | 154.84 | $\text{O}_3(g)$ | 238.92 |
| $\text{Kr}(g)$ | 164.08 | $\text{SO}_2(g)$ | 248.22 |
| C(graphite) | 5.69 | $\text{CH}_4(g)$ | 186.25 |
| C(diamond) | 2.4 | $\text{C}_2\text{H}_6(g)$ | 229.2 |
| $\text{CO}(g)$ | 197.66 | $\text{C}_3\text{H}_8(g)$ | 270.3 |
| $\text{CO}_2(g)$ | 213.6 | $\text{C}_2\text{H}_2(g)$ | 200.94 |
| $\text{HF}(g)$ | 173.78 | $\text{C}_2\text{H}_4(g)$ | 219.3 |
| $\text{HCl}(g)$ | 187.0 | $\text{C}_6\text{H}_6(l)$ | 173.2 |
| $\text{HBr}(g)$ | 198.70 | $\text{CH}_3\text{OH}(l)$ | 126.8 |
| $\text{HI}(g)$ | 206.3 | $\text{C}_2\text{H}_5\text{OH}(l)$ | 160.7 |
| $\text{H}_2\text{O}(g)$ | 188.84 | $\text{CH}_3\text{CHO}(l)$ | 263.8 |
| $\text{H}_2\text{O}(l)$ | 69.95 | $\text{HCOOH}(l)$ | 129.0 |
| $\text{NH}_3(g)$ | 192.77 | $\text{CH}_3\text{COOH}(l)$ | 159.8 |
| $\text{NO}(g)$ | 210.76 | $\text{C}_6\text{H}_{12}\text{O}_6(s)$ | 212.1 |
| $\text{N}_2\text{O}_4(g)$ | 304.38 | $\text{C}_{12}\text{H}_{22}\text{O}_{11}(s)$ | 360.2 |

larger standard entropy than methane. Both helium and neon are monatomic gases, so neither undergoes rotational or vibrational motions, but neon has a larger standard entropy than helium because its molar mass is greater. As we saw in the case of the one-dimensional particle-in-a box (Section 1.3), heavier atoms have more closely spaced energy levels, so there is a broader distribution of the energy of the atom among the energy levels. Consequently, there are more microstates associated with heavier atoms.

For simple molecules it is possible to calculate absolute entropies theoretically, and for most systems the theoretical value very closely agrees with third-law entropies calculated experimentally. However, in some situations the third-law entropy (determined using Equation 8.27 and accounting for any phase transitions) does not agree with the theoretical value. The origin of this discrepancy is generally due to defects or impurities that are frozen in the system at low temperatures. The third law does not apply for such a system because the system is not in its thermodynamically most stable state. The difference between the experimental entropy and the theoretical entropy for such a system is referred to as the **residual entropy**, which is *the value of the entropy at 0 K for systems for which the third law is not applicable*.

As an example, consider a crystal of carbon monoxide (CO). The dipole moment of CO is quite small (0.12 D) and carbon and oxygen are very similar in size, so the CO molecule is very nearly symmetrical. In a perfect crystal of CO [Figure 8.8(a)], the CO molecules are all aligned in an ordered fashion. However, because the two ends of the molecule are so similar, the molecules in a real crystal may be randomly oriented [Figure 8.8(b)].

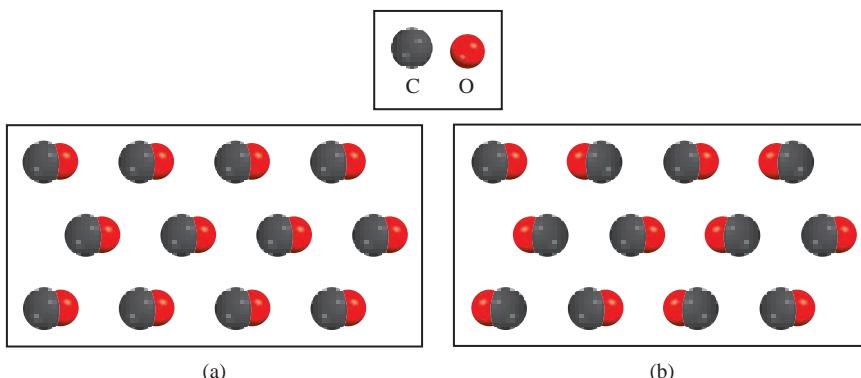


Figure 8.8 (a) Two-dimensional representation of the defect-free arrangement of crystalline carbon monoxide. The third law will hold for this crystal, and $S = 0$ at 0 K. (b) Two-dimensional arrangement of real crystalline carbon monoxide. Because of defects in orientation, this crystal will have a residual entropy, and $S > 0$ at 0 K.

If the orientation of the CO molecules is completely random, then each molecule has 2 possible orientations. Two molecules would have $2^2 = 4$ possibilities; three molecules would have $2^3 = 8$ possibilities, and so on. Using Boltzmann's formula (Equation 8.1) we can estimate the residual entropy for one mole ($N = N_A$) of CO molecules as

$$\begin{aligned} S_{\text{res}} &= k_B \ln W \\ &= k_B \ln 2^{N_A} = k_B N_A \ln 2 = R \ln 2 \\ &= (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln 2 \\ &= 5.8 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

where we have used $R = k_B N_A$. The experimental value of the residual entropy for CO is about $4.2 \text{ J mol}^{-1} \text{ K}^{-1}$. This value is slightly lower than the estimate from Boltzmann's formula, so the orientation of the CO molecules in the crystal is not completely random.

Entropy of Reaction

Suppose that the system is represented by the following chemical reaction:



Analogous to the standard enthalpy change of a reaction (see Equation 7.41), the **standard entropy change of reaction** is given by *the difference in standard entropies between the products and reactants*:

$$\Delta S_{\text{rxn}}^\circ = [c S^\circ(C) + d S^\circ(D)] - [a S^\circ(A) + b S^\circ(B)] \quad (8.22)$$

We can generalize Equation 8.22 as:

$$\Delta S_{\text{rxn}}^\circ = \sum_{\text{products}} v_p S^\circ(\text{products}) - \sum_{\text{reactants}} v_r S^\circ(\text{reactants}) \quad (8.23)$$

where v_p and v_r denote the stoichiometric coefficients for the reactants and products, and Σ (sigma) means “the sum of.” Note that in contrast to the standard enthalpy of formation, the standard entropy of an element in its most stable form is not zero, so all reactants and products (including elements) must be included in Equation 8.29.

Example 8.6 illustrates the calculation of $\Delta S_{\text{rxn}}^\circ$ from standard molar entropy data (Table 8.2 and Appendix 2).

Example 8.6

From the standard entropy values in Appendix 2, calculate the standard entropy changes for the following reactions at 25°C:

- $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$
- $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$
- $\text{H}_2(g) + \text{Cl}_2(g) \longrightarrow 2\text{HCl}(g)$

Strategy To calculate the standard entropy of a reaction, we look up the standard entropies of the reactants and products in Appendix 2 and apply Equation 8.23. As in the calculation of enthalpy of reaction [see Equation (7.41)], the stoichiometric coefficients have no units, so $\Delta S_{\text{rxn}}^{\circ}$ is expressed in units of $\text{J mol}^{-1} \text{K}^{-1}$.

Solution

$$\begin{aligned}\text{(a)} \quad \Delta S_{\text{rxn}}^{\circ} &= [S^{\circ}(\text{CaO}) + S^{\circ}(\text{CO}_2)] - [S^{\circ}(\text{CaCO}_3)] \\ &= [39.8 \text{ J mol}^{-1} \text{ K}^{-1} + 213.79 \text{ J mol}^{-1} \text{ K}^{-1}] - [92.9 \text{ J mol}^{-1} \text{ K}^{-1}] \\ &= 160.7 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

Thus, when 1 mole of CaCO_3 decomposes to form 1 mole of CaO and 1 mole of gaseous CO_2 , there is an increase in entropy equal to $160.7 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$\begin{aligned}\text{(b)} \quad \Delta S_{\text{rxn}}^{\circ} &= [2S^{\circ}(\text{NH}_3)] - [S^{\circ}(\text{N}_2) + 3S^{\circ}(\text{H}_2)] \\ &= (2)(192.77 \text{ J mol}^{-1} \text{ K}^{-1}) - [(191.61 \text{ J mol}^{-1} \text{ K}^{-1}) + (3)(130.68 \text{ J mol}^{-1} \text{ K}^{-1})] \\ &= -198.11 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

This result shows that when 1 mole of gaseous nitrogen reacts with 3 moles of gaseous hydrogen to form 2 moles of gaseous ammonia, there is a decrease in entropy equal to $198.11 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$\begin{aligned}\text{(c)} \quad \Delta S_{\text{rxn}}^{\circ} &= [2S^{\circ}(\text{HCl})] - [S^{\circ}(\text{H}_2) + S^{\circ}(\text{Cl}_2)] \\ &= (2)(186.90 \text{ J mol}^{-1} \text{ K}^{-1}) - [(130.68 \text{ J mol}^{-1} \text{ K}^{-1}) + (223.08 \text{ J mol}^{-1} \text{ K}^{-1})] \\ &= 20.04 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

Thus, the formation of 2 moles of gaseous HCl from 1 mole of gaseous H_2 and 1 mole of gaseous Cl_2 results in a small increase in entropy equal to $20.04 \text{ J mol}^{-1} \text{ K}^{-1}$.

Practice Exercise Calculate the standard entropy change for the following reactions at 25°C:

- $2\text{CO}(g) + \text{O}_2(g) \longrightarrow 2\text{CO}_2(g)$
- $3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$
- $2\text{NaHCO}_3(s) \longrightarrow \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$

The results of Example 8.6 are consistent with those observed for many other reactions. Taken together, they support the following general rules:

- ▶ If a reaction produces more gas molecules than it consumes [Example 8.6 (a)], $\Delta S_{\text{rxn}}^{\circ}$ is positive.
- ▶ If the total number of gas molecules diminishes [Example 8.6(b)], $\Delta S_{\text{rxn}}^{\circ}$ is negative.
- ▶ If there is no net change in the total number of gas molecules [Example 8.6(c)], then $\Delta S_{\text{rxn}}^{\circ}$ may be positive or negative, but it will be relatively small numerically.

These conclusions make sense, given that gases invariably have greater entropy than liquids and solids. For reactions involving only liquids and solids, predicting the sign of $\Delta S_{\text{rxn}}^{\circ}$ is more difficult, but in many such cases an increase in the total number of molecules and/or ions is accompanied by an increase in entropy.

Example 8.7 shows how knowing the nature of reactants and products makes it possible to predict entropy changes.

Example 8.7

Predict whether the entropy change of the system in each of the following reactions is positive or negative:

- $2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l)$
- $\text{NH}_4\text{Cl}(s) \longrightarrow \text{NH}_3(g) + \text{HCl}(g)$
- $\text{H}_2(g) + \text{Br}_2(g) \longrightarrow 2\text{HBr}(g)$

Strategy We are asked to predict, not calculate, the sign of the entropy change in the reactions. The factors that lead to an increase in entropy are: (1) a transition from a condensed phase to the vapor phase and (2) a reaction that produces more product molecules than reactant molecules in the same phase. It is also important to compare the relative complexity of the product and reactant molecules. In general, the more complex the molecular structure, the greater the entropy of the compound.

- Solution**
- Two gaseous reactant molecules combine to form one liquid product molecule. Even though H_2O is more complex structurally than either H_2 or O_2 , the net decrease of one molecule and conversion of gases to a liquid decreases the number of microstates; hence, $\Delta S_{\text{rxn}}^{\circ}$ is negative.
 - A solid reactant is converted to two gaseous products. Therefore, $\Delta S_{\text{rxn}}^{\circ}$ is positive.
 - Two diatomic gas molecules combine to form two different diatomic gas molecules. Thus, the number of reactant molecules is the same as the number of product molecules and both the reactants and products are of similar complexity (that is, all are diatomic). As a result, we cannot easily predict the sign of $\Delta S_{\text{rxn}}^{\circ}$, but the magnitude of the change must be quite small.

Practice Exercise Discuss qualitatively the sign of the entropy change expected for each of the following processes:

- $\text{I}_2(s) \longrightarrow 2\text{I}(g)$
- $2\text{Zn}(s) + \text{O}_2(g) \longrightarrow 2\text{ZnO}(s)$
- $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2\text{NO}(g)$

Temperature Dependence of Standard Entropy Changes

For most substances, the values of standard entropies are not available for a wide range of temperatures. Most commonly, tables present only data at 25°C. For most purposes, it is sufficient to use the standard entropies at 25°C to calculate reaction entropy changes at other temperatures because ΔS_{rxn} does not generally depend highly on temperature. If accurate work is needed, however, or if the temperature of interest is well removed from the temperature for which data are available, it is necessary to correct the tabulated values for the change in temperature. To do this, we can use a procedure analogous to that outlined in Section 7.7 for the calculation of ΔH_{rxn} at alternate temperatures.

Like enthalpy, the change in entropy due to temperature change is governed by the heat capacity. Because standard entropies are defined as being at fixed pressure (1 bar), we can use Equation 8.18 to determine the value of the standard entropy at a temperature T_2 relative to its known value at temperature T_1 :

$$S_f^\circ(T_2) = S_f^\circ(T_1) + \bar{C}_P \ln \frac{T_2}{T_1}$$

assuming that the standard constant pressure molar heat capacity, \bar{C}_P° , is temperature independent. Substituting this expression for $S_f^\circ(T_2)$ into Equation 8.23 and using algebra similar to that used to derive Equation 7.49 for reaction enthalpy changes, yields

$$\Delta S_{\text{rxn}}^\circ(T_2) = \Delta S_{\text{rxn}}^\circ(T_1) + \Delta \bar{C}_{P,\text{rxn}}^\circ \ln \frac{T_2}{T_1} \quad (8.24)$$

where $\Delta \bar{C}_{P,\text{rxn}}^\circ$ is defined as in Equation 7.50:

$$\Delta C_{P,\text{rxn}}^\circ = \sum_{\text{products}} v_P \bar{C}_P^\circ - \sum_{\text{reactants}} v_R \bar{C}_P^\circ$$

Equation 8.24 describes the temperature dependence of the reaction entropy change and is analogous to Kirchhoff's law for the temperature dependence of the reaction enthalpy change (Equation 7.49).

Example 8.8 shows how to use Equation 8.24 to calculate the standard entropy change for a reaction that occurs well above 25°C.

Example 8.8

The standard entropy change for the reaction



is $-137.2 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K and 1 bar. Calculate the value of $\Delta S_{\text{rxn}}^\circ$ at 380 K, assuming that all \bar{C}_P° values are independent of temperature.

Strategy To use Equation 8.30, we need $\Delta \bar{C}_{P,\text{rxn}}^\circ$ for this reaction. This value was calculated to be $-9.8 \text{ kJ mol}^{-1} \text{ K}^{-1}$ in Example 7.13 using data from Appendix 2 and Equation 7.50.

Solution We are given $\Delta S_{\text{rxn}}^\circ$ in the problem statement and $\Delta \bar{C}_{P,\text{rxn}}^\circ$ in Example 7.13, so using Equation 8.24 gives

$$\begin{aligned} \Delta S_{\text{rxn}}^\circ(T_2) &= \Delta S_{\text{rxn}}^\circ(T_1) + \Delta \bar{C}_{P,\text{rxn}}^\circ \ln \frac{T_2}{T_1} \\ &= -137.2 \text{ J mol}^{-1} \text{ K}^{-1} + (-9.8 \text{ J mol}^{-1} \text{ K}^{-1}) \ln \frac{380 \text{ K}}{298 \text{ K}} \\ &= -139.6 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

Practice Exercise Using data from Appendix 2, calculate $\Delta S_{\text{rxn}}^\circ$ for the reaction



at 450 K.

8.4 | The Spontaneity of a Process at Constant Temperature and Pressure Is Governed by the Gibbs Free Energy

The second law of thermodynamics tells us that a spontaneous reaction increases the entropy of the universe, that is, $\Delta S_{\text{univ}} > 0$. In order to determine the sign of ΔS_{univ} for a reaction, however, we would need to calculate both ΔS_{sys} and ΔS_{surr} . In general, we are usually concerned only with what happens in a particular system and not

with the entire universe. Therefore, we need another thermodynamic function to help us determine whether a reaction will occur spontaneously if we consider only the system itself.

Spontaneity in Nonisolated Systems: Gibbs Free Energy

When a isothermal process occurs in a system that is not isolated, but is instead coupled to its surroundings, we cannot apply the second law of thermodynamics directly to the system alone. Instead, we must consider the total entropy change in the universe, which from Equations 8.4 and 8.5 is given by

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

Because the surroundings are so much bigger than the system, we can assume that the surroundings are unperturbed by the transfer of heat, so the transfer can be considered to be reversible. This reversibility combined with the condition that T is constant implies that $\Delta S_{\text{surr}} = q_{\text{surr}}/T$ (Equation 8.8), giving

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \geq 0$$

Because $q_{\text{sys}} = -q_{\text{surr}}$, we have

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{q_{\text{sys}}}{T} \geq 0 \quad (8.25)$$

If we make a further assumption that the process occurs at constant pressure, then

$$\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} \geq 0 \quad (8.26)$$

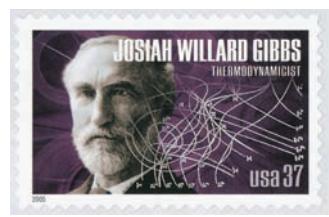
because $q_{\text{sys}} = \Delta H_{\text{sys}}$ for a constant pressure process (Equation 7.13). Thus, an exothermic process ($\Delta H_{\text{sys}} < 0$) will increase the entropy of the surroundings ($\Delta S_{\text{surr}} > 0$), and an endothermic process ($\Delta H_{\text{sys}} > 0$) will decrease the entropy of the surroundings ($\Delta S_{\text{surr}} < 0$) (Figure 8.9). Any spontaneous process that occurs in a nonisolated system at constant T and P must satisfy Equation 8.26. For convenience, we can multiply Equation 8.26 above by $-T$ to obtain

$$\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} \leq 0 \quad (8.27)$$

Equation 8.27 is useful because it only requires information about the system, eliminating the need to consider the surroundings specifically. In order to express the spontaneity of a process more directly, we introduce a new thermodynamic function called the **Gibbs free energy** (G) (after the American physicist Josiah Willard Gibbs⁷) as

$$G = H - TS \quad (8.28)$$

7. Josiah Willard Gibbs (1839–1903). American physicist. One of the founders of thermodynamics and statistical mechanics, Gibbs was a modest and private individual who spent most of his professional life at Yale University. Because he published most of his works in obscure journals, Gibbs never gained the eminence that his contemporary and admirer James Clerk Maxwell enjoyed. Even today, very few people outside of chemistry and physics have ever heard of Gibbs.



A 2005 commemorative stamp honoring Gibbs

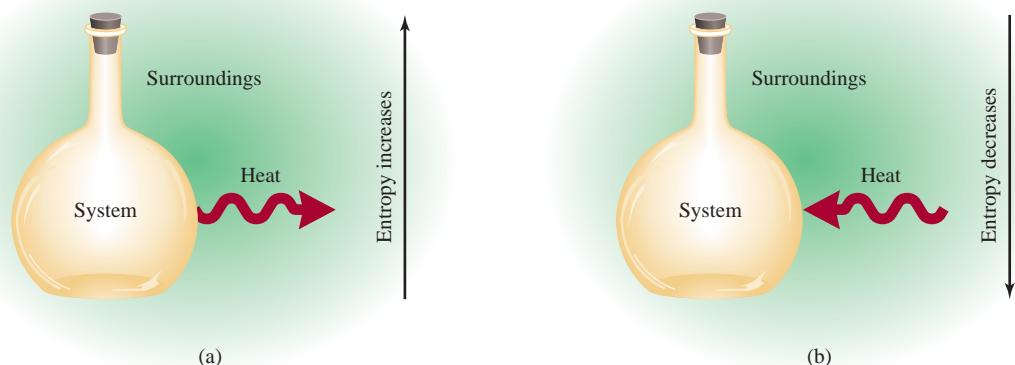


Figure 8.9 (a) An exothermic process transfers heat from the system to the surroundings and results in an increase in the entropy of the surroundings. (b) An endothermic process absorbs heat from the surroundings and thereby decreases the entropy of the surroundings.

Like both H and TS , G has units of energy. Also, because H , T , and S are all state functions, G is also a state function.

The change in the Gibbs free energy (ΔG) for a constant temperature process is

$$\Delta G = \Delta H - T\Delta S \quad (8.29)$$

From Equations 8.27 and 8.29, we see that the spontaneity criterion for process occurring under constant pressure and temperature conditions is

$$\Delta G \leq 0 \quad (8.30)$$

($\Delta G < 0$ holds for a spontaneous process and $\Delta G = 0$ for a reversible (or equilibrium) process.) Because G , H , T , and S are state functions, Equations 8.27 and 8.30 hold even if the temperature and pressure are not strictly constant throughout the process as long as the initial and final states are at the same temperature and pressure.

Gibbs Free Energy and Nonexpansion Work

Equation 8.30 provides an extremely useful criterion for determining the direction of spontaneous changes and the nature of physical and chemical equilibrium. In addition, the changes in the Gibbs free energy function enable us to determine the amount of work that can be done in a process at constant temperature and pressure. To see this, start with the expression for ΔG for a process at constant temperature and pressure (Equation 8.29):

$$\Delta G = \Delta H - T\Delta S = \Delta U + P\Delta V - T\Delta S \quad (8.31)$$

where we have used the fact that $\Delta H = \Delta U + P\Delta V$ at constant pressure (Equation 7.12). The second law of thermodynamics, in the form of the Clausius inequality (Equation 8.9), states that for any isothermal process $q \leq T\Delta S$. Combining this inequality with Equation 8.31 gives

$$\Delta G \geq \Delta U + P\Delta V - q$$

Using the first law of thermodynamics (Equation 7.4), we can replace ΔU with $q + w$ to give

$$\begin{aligned}\Delta G &\geq q + w + P\Delta V - q \\ \Delta G &\geq w + P\Delta V\end{aligned}$$

The quantity $P\Delta V$ represents the work delivered by the system due to expansion, so the quantity $w_{\text{delivered}} - P\Delta V$ represents that part of the work delivered by the system that is not due to expansion. Thus, the maximum nonexpansion work, $w_{\text{delivered, nonexp}}$, that can be delivered by a system in a process at constant temperature and pressure is equal to the *decrease* in the Gibbs free energy of the process, that is,

$$w_{\text{delivered, nonexp}} \leq -\Delta G \quad (8.32)$$

where the equality holds only if the process is reversible.⁸ Equation 8.31 is very important in electrochemistry (Chapter 13) because the electrical work that is produced by the chemical reactions in electrochemical cells, such as batteries, is a type of nonexpansion work.

The word *free* in *free energy* does not mean "without cost," but instead refers to amount of energy "available" to do work.

Standard Gibbs Free-Energy Changes

The **standard Gibbs free energy of reaction** ($\Delta G_{\text{rxn}}^{\circ}$) is the Gibbs free energy change for a reaction that occurs under standard-state conditions when reactants in their standard states are converted to products in their standard states. The calculation of $\Delta G_{\text{rxn}}^{\circ}$ is very similar to that for $\Delta H_{\text{rxn}}^{\circ}$ (Section 7.4). We start with the generic reaction



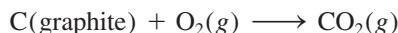
The standard Gibbs free energy change for this reaction is given by

$$\Delta G_{\text{rxn}}^{\circ} = [c\Delta G_f^{\circ}(C) + d\Delta G_f^{\circ}(D)] - [a\Delta G_f^{\circ}(A) + b\Delta G_f^{\circ}(B)] \quad (8.33)$$

or, in general,

$$\Delta G_{\text{rxn}}^{\circ} = \sum_{\text{products}} v_p \Delta G_f^{\circ}(\text{products}) - \sum_{\text{reactants}} v_R \Delta G_f^{\circ}(\text{reactants}) \quad (8.34)$$

where v_p and v_R are the stoichiometric coefficients of the products and reactants, respectively. The ΔG_f° term is the **standard Gibbs free energy of formation** of a compound, that is, the Gibbs free-energy change that occurs when 1 mole of the compound is synthesized from its elements in their standard states. For the combustion of graphite,



8. In addition to the Gibbs free energy, another similar thermodynamic state function commonly used in thermodynamics is the *Helmholtz free energy* (A), defined as $A = U - TS$. At constant temperature, the change in the Helmholtz free energy is given by $\Delta A = \Delta U - T\Delta S$. In analogy to Equation 8.32, the maximum total work that can be delivered by a system in a constant-temperature process is equal to the negative of the change in the Helmholtz energy: $w_{\text{delivered}} \leq -\Delta A$. The Helmholtz free energy is important because it gives the criterion for spontaneity for processes at constant temperature and *volume*, that is, for any spontaneous process at constant T and V , the change in the Helmholtz free energy must be negative: $\Delta A < 0$. In chemistry, the Gibbs free energy is used far more often than the Helmholtz free energy because most processes of chemical interest occur under constant-pressure (and not constant-volume) conditions.

the standard free-energy change [from Equation 8.34] is

$$\Delta G_{\text{rxn}}^{\circ} = \Delta G_f^{\circ}(\text{CO}_2) - [\Delta G_f^{\circ}(\text{C, graphite}) + \Delta G_f^{\circ}(\text{O}_2)]$$

As in the case of the standard enthalpy of formation (Section 7.4), we define the standard Gibbs free energy of formation of any element in its stable allotropic form at 1 bar and 25°C as zero. Thus,

$$\Delta G_f^{\circ}(\text{C, graphite}) = 0 \quad \text{and} \quad \Delta G_f^{\circ}(\text{O}_2) = 0$$

Therefore, the standard Gibbs free-energy change for the combustion of graphite equals the standard free energy of formation of CO₂:

$$\Delta G_{\text{rxn}}^{\circ} = \Delta G_f^{\circ}(\text{CO}_2)$$

Elements not in their most stable form will have nonzero Gibbs free energies of formation. For example, carbon in the form of diamond has a nonzero Gibbs free energy of formation [$\Delta G_f^{\circ}(\text{diamond}) = 2.87 \text{ kJ mol}^{-1}$] at 25°C, which represents the standard Gibbs free energy change for the conversion of graphite to diamond at that temperature. Appendix 2 lists the values of ΔG_f° for a number of substances.

In the event that tables for standard Gibbs energies of formation are not readily available, we can also obtain the Gibbs free energy of the reaction by first determining the standard enthalpy change of a reaction using the methods discussed in Section 7.4 and the standard entropy change for the reaction as discussed in Section 8.3. Once $\Delta H_{\text{rxn}}^{\circ}$ and $\Delta S_{\text{rxn}}^{\circ}$ are known, $\Delta G_{\text{rxn}}^{\circ}$ can be calculated using Equation 8.29 applied to standard states:

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T\Delta S_{\text{rxn}}^{\circ} \quad (8.35)$$

Example 8.9 shows how to calculate standard Gibbs free energy changes.

Example 8.9

Calculate the standard Gibbs free energy changes for the following reactions at 25°C:

- (a) $\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$
- (b) $2\text{MgO}(s) \longrightarrow 2\text{Mg}(s) + \text{O}_2(g)$

Strategy To calculate the standard Gibbs free energy change of a reaction, we look up the standard free energies of formation of reactants and products in Appendix 2 and use these values in Equation 8.40. Remember that ΔG_f° for elements such as O₂(g) and Mg(s) is zero because they are stable allotropes of their respective elements at 1 bar and 25°C. Check that the chemical equations are balanced so that you use the correct stoichiometric coefficients in Equation 8.40. Finally, all stoichiometric coefficients are unitless, so $\Delta G_{\text{rxn}}^{\circ}$ is expressed in units of kJ mol⁻¹.

Solution

- (a) According to Equation 8.40,

$$\Delta G_{\text{rxn}}^{\circ} = [\Delta G_f^{\circ}(\text{CO}_2) + 2\Delta G_f^{\circ}(\text{H}_2\text{O})] - [\Delta G_f^{\circ}(\text{CH}_4) + 2\Delta G_f^{\circ}(\text{O}_2)]$$

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Inserting the appropriate values from Appendix 2 gives

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= [(-394.4 \text{ kJ mol}^{-1}) + (2)(-237.1 \text{ kJ mol}^{-1})] \\ &\quad - [(-50.8 \text{ kJ mol}^{-1}) + (2)(0 \text{ kJ mol}^{-1})] \\ &= -817.8 \text{ kJ mol}^{-1}\end{aligned}$$

(b) The equation is

$$\Delta G_{\text{rxn}}^{\circ} = [2\Delta G_f^{\circ}(\text{Mg}) + \Delta G_f^{\circ}(\text{O}_2)] - [2\Delta G_f^{\circ}(\text{MgO})]$$

Plugging in the data from Appendix 2 yields

$$\begin{aligned}\Delta G_{\text{rxn}}^{\circ} &= [(2)(0 \text{ kJ mol}^{-1}) + (0 \text{ kJ mol}^{-1})] - [(2)(-569.6 \text{ kJ mol}^{-1})] \\ &= +1139 \text{ kJ mol}^{-1}\end{aligned}$$

Practice Exercise Calculate the standard free-energy changes for the following reactions at 25°C:

- (a) $\text{H}_2(g) + \text{Br}_2(l) \longrightarrow 2\text{HBr}(g)$
- (b) $2\text{C}_2\text{H}_6(g) + 7\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(l)$

At this point, it is useful to distinguish between ΔG and ΔG° . In any given experiment, it is rare for the reactants and products to all be present at their standard-state pressures or concentrations. Even if the reaction is set up initially under standard-state conditions for all substances involved, as the reaction proceeds to equilibrium, the system may evolve to non-standard-state conditions. Under these conditions, it is the sign of ΔG not ΔG° that predicts the direction of the reaction. As discussed in Chapter 10, however, the sign of ΔG° does indicate whether the reactants or the products are favored when the reacting system reaches equilibrium.

Temperature Dependence of ΔG

In all but the most accurate work, it is usually a good approximation to assume that ΔH and ΔS are constant for a chemical reaction even if the temperature changes. The Gibbs free energy change (ΔG) generally depends strongly upon temperature, however, as was shown by Equation 8.29

$$\Delta G = \Delta H - T\Delta S$$

Thus, the magnitude and sign of ΔG as a function of temperature depends upon the relative magnitudes of ΔH and ΔS . Based on Equation 8.29, the change in ΔG with temperature primarily depends on the sign of ΔS . If $\Delta S > 0$, then ΔG will *decrease* with increasing temperature, and if $\Delta S < 0$, ΔG will *increase* with increasing temperature. Based on the signs of ΔH and ΔS , there are four possibilities for ΔG :

- If ΔH and ΔS are both positive, then ΔG will be positive at low temperatures (where enthalpy dominates) and become negative at high temperatures (where entropy dominates). The temperature at which ΔG crosses over from positive to negative (that is, when $\Delta H = T \Delta S$) depends upon the relative magnitudes of ΔH and ΔS . For example: $2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$; $\Delta H^{\circ} = 181.6 \text{ kJ mol}^{-1}$, $\Delta S^{\circ} = 219.3 \text{ J mol}^{-1}$.

- ▶ If ΔH is positive and ΔS is negative, ΔG will always be positive regardless of temperature. For example: $3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$; $\Delta H^\circ = 285.4 \text{ kJ mol}^{-1}$, $\Delta S^\circ = -137.5 \text{ J mol}^{-1}$.
- ▶ If ΔH is negative and ΔS is positive, ΔG will always be negative regardless of temperature. For example: $2\text{H}_2\text{O}_2(l) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$; $\Delta H^\circ = -196.5 \text{ kJ mol}^{-1}$, $\Delta S^\circ = 166.8 \text{ J mol}^{-1}$.
- ▶ If both ΔH and ΔS are both negative, then ΔG will be negative at low temperatures and become positive at high temperatures. The temperature at which ΔG crosses over from negative to positive depends upon the relative magnitude of ΔH and ΔS . For example: $\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$; $\Delta H^\circ = -177.0 \text{ kJ mol}^{-1}$, $\Delta S^\circ = -285.11 \text{ J mol}^{-1}$.

As an example, consider the preparation of calcium oxide (CaO), also called quicklime. Calcium oxide is an extremely valuable inorganic substance used in steel-making, the production of calcium metal, the paper industry, water treatment, and pollution control. It is prepared industrially on a large scale by decomposing limestone (CaCO_3) in a kiln at a high temperature:



The reaction is reversible, and CaO readily combines with CO_2 to form CaCO_3 . The pressure of CO_2 in equilibrium with CaCO_3 and CaO increases with temperature. In the industrial preparation of quicklime, the system is never maintained at equilibrium; rather, CO_2 is constantly removed from the kiln to shift the equilibrium from left to right, promoting the formation of calcium oxide.

The important information for the practical chemist to know is the temperature at which the decomposition of CaCO_3 becomes appreciable (that is, the temperature at which the reaction begins to favor products). We can make a reliable estimate of that temperature as follows. First, use the data in Appendix 2 to calculate ΔH° and ΔS° for the reaction at 25°C . Using Equation 7.41 to determine ΔH° :

$$\begin{aligned}\Delta H^\circ &= [\Delta H_f^\circ(\text{CaO}) + \Delta H_f^\circ(\text{CO}_2)] - [\Delta H_f^\circ(\text{CaCO}_3)] \\ &= [(-634.9 \text{ kJ mol}^{-1}) + (-393.5 \text{ kJ mol}^{-1})] - (-1207.6 \text{ kJ mol}^{-1}) \\ &= 179.2 \text{ kJ mol}^{-1}\end{aligned}$$

Next, use Equation 8.23 to determine ΔS°

$$\begin{aligned}\Delta S^\circ &= [S^\circ(\text{CaO}) + S^\circ(\text{CO}_2)] - S^\circ(\text{CaCO}_3) \\ &= [38.1 \text{ J K}^{-1} \text{ mol}^{-1} + 213.6 \text{ J mol}^{-1} \text{ K}^{-1}] - 91.7 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 160.0 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

From Equation 8.35

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

we obtain

$$\begin{aligned}\Delta G^\circ &= 179.2 \text{ kJ mol}^{-1} - (298 \text{ K})(160.0 \text{ J mol}^{-1} \text{ K}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\ &= 131.5 \text{ kJ mol}^{-1}\end{aligned}$$

Because ΔG° is a large positive quantity, products are not favored for this reaction at 25°C (298 K). Indeed, the pressure of CO_2 is so low at room temperature that it cannot be measured.

In order to make ΔG° negative, we first have to find the temperature at which ΔG° is zero, that is,

$$0 = \Delta H^\circ - T\Delta S^\circ$$

or

$$\begin{aligned} T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\ &= \frac{(179.2 \text{ kJ mol}^{-1})(1000 \text{ J kJ}^{-1})}{160.0 \text{ J mol}^{-1} \text{ K}^{-1}} \\ &= 1120 \text{ K or } 830^\circ\text{C} \end{aligned}$$

At a temperature higher than 847°C , ΔG° becomes negative, indicating that the reaction now favors the formation of CaO and CO₂. At 860°C (1133 K), for example,

$$\begin{aligned} \Delta G^\circ &= 179.2 \text{ kJ mol}^{-1} - (1133 \text{ K})(160.0 \text{ J mol}^{-1} \text{ K}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\ &= -2.1 \text{ kJ mol}^{-1} \end{aligned}$$

Note that we used the ΔH° and ΔS° values at 25°C to calculate the changes that occur at a much higher temperature. Because both ΔH° and ΔS° change with temperature, this approach will not yield an accurate value of ΔG° , but it is good enough for a rough estimate. Additionally, do not be misled into thinking that nothing happens below 847°C and that at 847°C CaCO₃ suddenly begins to decompose. Just because ΔG° is positive at some temperature below 847°C does not mean that CO₂ is not produced; on the contrary, it means that the pressure of the CO₂ gas formed at that temperature will be below 1 bar (its standard-state value). As Figure 8.10 shows, the pressure of CO₂ at first increases very slowly with temperature and becomes easily measurable above 700°C . The significance of 847°C is that this is the temperature at which the equilibrium pressure of CO₂ reaches 1 bar. Above 847°C , the equilibrium pressure of CO₂ exceeds 1 bar.

Example 8.10

For the reaction NH₃(g) + HCl(g) \longrightarrow NH₄Cl(s), calculate ΔG° at 25°C and 1000°C . At what temperature (if any) does ΔG° become zero? Assume that ΔH° and ΔS° are independent of temperature.

Strategy First determine ΔH° and ΔS° using Equation 7.41 and 8.26, respectively, and the data in Appendix 2. Then ΔG° can be calculated at the two temperatures using Equation 8.35.

Solution Plugging the appropriate ΔH_f° values from Appendix 2 into Equation 7.41 yields

$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ(\text{NH}_4\text{Cl}) - [\Delta H_f^\circ(\text{NH}_3) + \Delta H_f^\circ(\text{HCl})] \\ &= -314.4 \text{ kJ mol}^{-1} - [-45.9 \text{ kJ mol}^{-1} + (-92.3 \text{ kJ mol}^{-1})] \\ &= -176.2 \text{ kJ mol}^{-1} \end{aligned}$$

Similarly, plugging the appropriate S° values into Equation 8.23 yields

$$\begin{aligned} \Delta S^\circ &= S^\circ(\text{NH}_4\text{Cl}) - [S^\circ(\text{NH}_3) + S^\circ(\text{HCl})] \\ &= 94.6 \text{ J mol}^{-1} \text{ K}^{-1} - [192.8 \text{ J mol}^{-1} \text{ K}^{-1} + 187.0 \text{ J mol}^{-1} \text{ K}^{-1}] \\ &= -285.2 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

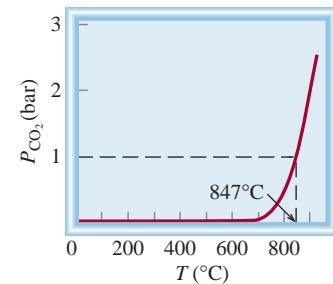


Figure 8.10 The equilibrium pressure of CO₂ from the decomposition of CaCO₃, as a function of temperature. This curve is calculated by assuming that ΔH° and ΔS° of the reaction do not change with temperature.

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Equation 8.38 then gives the following for ΔG° at 25°C and at 1000°C:

$$\begin{aligned}\Delta G^\circ(25^\circ\text{C}) &= -176.2 \text{ kJ mol}^{-1} - (298.15 \text{ K})(-285.2 \text{ J mol}^{-1} \text{ K}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\ &= -91.32 \text{ kJ mol}^{-1} \\ \Delta G^\circ(1000^\circ\text{C}) &= -176.2 \text{ kJ mol}^{-1} - (1273.15 \text{ K})(-285.2 \text{ J mol}^{-1} \text{ K}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\ &= +186.9 \text{ kJ mol}^{-1}\end{aligned}$$

The temperature at which ΔG° is zero can be found using the same method used for the decomposition of CaCO_3 :

$$\begin{aligned}T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\ &= \frac{(-176.2 \text{ kJ mol}^{-1})(1000 \text{ J kJ}^{-1})}{-285.2 \text{ J mol}^{-1} \text{ K}^{-1}} \\ &= 618 \text{ K or } 347^\circ\text{C}\end{aligned}$$

Check Because both ΔH° and ΔS° are negative, ΔG° should be negative at low temperatures and positive at sufficiently high temperatures. This is consistent with the values calculated at 25°C and 1000°C.

Practice Exercise For the reaction $2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$, calculate ΔG° at 25°C and 800°C. At what temperature (if any) does ΔG° become zero? Assume that ΔH° and ΔS° are independent of temperature.

In some cases, if accurate work is required, it is necessary to take into account the temperature dependence of ΔH° and ΔS° in the calculation of ΔG° at temperatures other than that assumed in the data tables (usually 25°C). The most straightforward method to determine the effect of temperature change on ΔG° is to use Kirchhoff's law (Equation 7.49) to calculate ΔH° at the new temperature and to use Equation 8.24 to calculate ΔS° . Then, use these values for ΔH° and ΔS° in Equation 8.35 to calculate the new value of ΔG° . Example 8.11 shows how this is done.

Example 8.11

For the reaction $2\text{NO}_2(g) \longrightarrow \text{N}_2\text{O}_4(g)$, use the data in Appendix 2 to determine the temperature at which $\Delta G^\circ = 0$, assuming that ΔH° and ΔS° are temperature independent. To estimate the error caused by this assumption, use the heat capacity data in Appendix 2 to better estimate ΔG° at this temperature.

Strategy The first part of the calculation proceeds in a similar fashion as Example 8.10. That is, determine ΔH° and ΔS° using Equations 7.41 and 8.23, respectively, and the data in Appendix 2. Then, use these values of ΔH° and ΔS° to calculate the temperature at which ΔG° should equal zero by setting Equation 8.35 equal to zero and solving for T . Next, use this value for T in Equation 7.49 (Kirchhoff's law) and Equation 8.24 to calculate the corrections in ΔH° and ΔS° , respectively, due to the nonzero heat capacity. Both Kirchhoff's law (Equation 7.49) for the temperature dependence of enthalpy change and the corresponding equation (Equation 8.24) for entropy change require the calculation of $\Delta \bar{C}_P$ using Equation 7.50. Finally, use these new values of ΔH° and ΔS° in Equation 8.35 to calculate a more accurate value of ΔG° at T .

—Continued

Continued—

Solution Plugging the appropriate ΔH_f° from Appendix 2 into Equation 7.41 yields

$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\text{N}_2\text{O}_4) - 2\Delta H_f^\circ(\text{NO}_2) \\ &= 9.66 \text{ kJ mol}^{-1} - 2(33.85 \text{ kJ mol}^{-1}) \\ &= -58.04 \text{ kJ mol}^{-1}\end{aligned}$$

Similarly, plugging the appropriate S° values into Equation 8.23 yields

$$\begin{aligned}\Delta S^\circ &= S^\circ(\text{N}_2\text{O}_4) - 2S^\circ(\text{NO}_2) \\ &= 304.3 \text{ J mol}^{-1} \text{ K}^{-1} - 2(240.46 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= -176.6 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

The temperature at which ΔG° is zero can be found, as in Example 8.10

$$\begin{aligned}T &= \frac{\Delta H^\circ}{\Delta S^\circ} \\ &= \frac{(-58.04 \text{ kJ mol}^{-1})(1000 \text{ J kJ}^{-1})}{-176.6 \text{ J mol}^{-1} \text{ K}^{-1}} \\ &= 328.6 \text{ K or } 55.5^\circ\text{C}\end{aligned}$$

To get a better estimate of ΔG° at this temperature, we need to calculate the corrections in ΔH° and ΔS° due to the nonzero heat capacity using Equations 7.49 (Kirchhoff's law) and 8.33, respectively. We need $\Delta \bar{C}_P$ for both of these equations, which can be obtained using Equation 7.50 as follows:

$$\begin{aligned}\Delta \bar{C}_P &= \bar{C}_P(\text{N}_2\text{O}_4) - 2\bar{C}_P(\text{NO}_2) \\ &= 79.2 \text{ J mol}^{-1} \text{ K}^{-1} - 2(37.2 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= -4.8 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

Using Kirchhoff's law (Equation 7.49), we have

$$\begin{aligned}\Delta H^\circ(325.5 \text{ K}) &= \Delta H^\circ(298.15 \text{ K}) + \Delta \bar{C}_P(325.5 \text{ K} - 298.15 \text{ K}) \\ &= -58.04 \text{ kJ mol}^{-1} + (+4.8 \text{ J K}^{-1} \text{ mol}^{-1})(27.35 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \\ &= -57.91 \text{ kJ mol}^{-1}\end{aligned}$$

Equation 8.33 gives the new entropy change:

$$\begin{aligned}\Delta S^\circ(328.6 \text{ K}) &= \Delta S^\circ(298.15 \text{ K}) + \Delta \bar{C}_P \ln \frac{325.5 \text{ K}}{298.15 \text{ K}} \\ &= -176.6 \text{ J K}^{-1} \text{ mol}^{-1} + (+4.8 \text{ J mol}^{-1} \text{ K}^{-1}) \ln (1.092) \\ &= -176.2 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

With these new values for ΔH° and ΔS° we can calculate ΔG° at 328.6 K using Equation 8.38:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -57.91 \text{ kJ mol}^{-1} - 328.6 \text{ K} (-176.2 \text{ J K}^{-1} \text{ mol}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\ &= -0.011 \text{ kJ mol}^{-1}\end{aligned}$$

Comment If entropy and enthalpy changes are temperature independent, then $\Delta G^\circ = 0$ at 325.5 K for the reaction in this problem. If we account for the temperature dependence of ΔH° and ΔS° , then we find that ΔG° is slightly negative at this temperature. Because both ΔH° and ΔS° are negative, ΔG° will be negative at low temperatures and positive at high temperatures. Because ΔG° is negative at 328.6 K, then that temperature must be slightly too low.

—Continued

The Thermodynamics of a Rubber Band

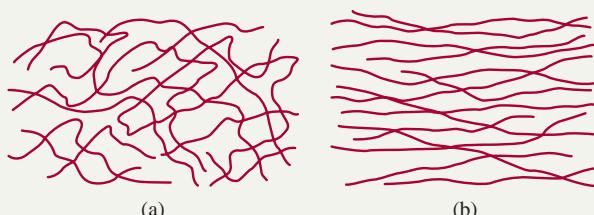
The common rubber band has some very interesting thermodynamic properties due to its molecular structure. To observe these properties, quickly stretch a rubber band (at least 0.5 cm wide) and then press it against your lips. You should feel a slight warming effect. Next, stretch a rubber band and hold it that way for a few seconds. Then quickly release the tension and press the rubber band against your lips again. This time you should feel a slight cooling effect. A thermodynamic analysis of these two experiments reveals a lot about the molecular structure of rubber.

Rearranging Equation 8.35 ($\Delta G = \Delta H - T\Delta S$) gives

$$T\Delta S = \Delta H - \Delta G$$

The warming effect (an exothermic process) due to stretching means that $\Delta H < 0$, and since stretching is nonspontaneous (that is, $\Delta G > 0$ and $-\Delta G < 0$), $T\Delta S$ must be negative, too. Because T , the absolute temperature, is always positive, the ΔS due to stretching must be negative. As a result, rubber in its natural state is more entangled (higher entropy) than when it is

under tension. When the tension is removed, the stretched rubber band spontaneously snaps back to its original shape, that is, ΔG is negative (so $-\Delta G$ is positive). The cooling effect means that it is an endothermic process ($\Delta H > 0$), so $T\Delta S$ is positive, too. Thus, the entropy of the rubber band increases when it goes from the stretched state to the natural state.



(a) Rubber molecules in their normal state. Note the high degree of entanglement and hence a large number of microstates (high entropy). (b) Under tension, the molecules line up in an orderly fashion and the number of microstates decreases (low entropy).

Continued—

Practice Exercise Use the data in Appendix 2 to determine the Gibbs free energy of formation, ΔG_f° , for CO at 400 K both with and without the assumption that ΔH° and ΔS° are independent of temperature. What is the percentage difference between the two values of ΔG_f° that you obtain?

8.5 | The Mixing of Pure Substances Leads to an Increase in the Entropy and a Decrease in the Gibbs Free Energy

Chemical reactions nearly always involve the mixing of two or more substances, so to understand the thermodynamics of a chemical reaction it is insufficient to know the entropy, enthalpy, and Gibbs free energy of the substances involved in their pure forms. We must also understand the thermodynamic consequences of mixing. We begin by examining the thermodynamics of mixing ideal gases.

Figure 8.11 shows a container in which n_A moles of ideal gas A at temperature T , pressure P , and volume V_A are separated by a partition from n_B moles of ideal gas B at the same temperature and pressure as gas A, but with volume V_B . When the partition is removed, the gases mix spontaneously and the entropy of the system increases. To calculate the entropy of mixing, ΔS_{mix} , we can treat the process as two separate isothermal ideal gas expansions using Equation 8.10. For gas A:

$$\Delta S_A = n_A R \ln \frac{V_A + V_B}{V_A}$$

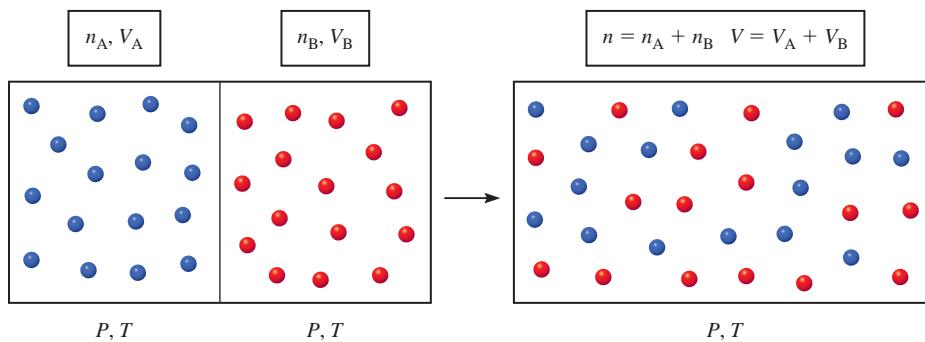


Figure 8.11 When two ideal gases at the same temperature and pressure are mixed, an increase in the entropy, called the entropy of mixing, is observed.

For gas B:

$$\Delta S_B = n_B R \ln \frac{V_A + V_B}{V_B}$$

(We can treat these expansions separately because the two gases are ideal and do not interact. That is, each gas expands without being affected by the presence of the other gas.) Thus, we have

$$\Delta S_{\text{mix}} = \Delta S_A + \Delta S_B = n_A R \ln \frac{V_A + V_B}{V_A} + n_B R \ln \frac{V_A + V_B}{V_B}$$

According to Avogadro's law (Equation 5.17), the volume of an ideal gas is directly proportional to the number of moles of the gas at constant T and P , so the previous equation can be rewritten as

$$\begin{aligned} \Delta S_{\text{mix}} &= n_A R \ln \frac{n_A + n_B}{n_A} + n_B R \ln \frac{n_A + n_B}{n_B} \\ &= -n_A R \ln \frac{n_A}{n_A + n_B} + n_B R \ln \frac{n_B}{n_A + n_B} \\ &= -n_A R \ln x_A + n_B R \ln x_B \\ \Delta S_{\text{mix}} &= -R(n_A \ln x_A + n_B \ln x_B) \end{aligned} \tag{8.36}$$

where x_A and x_B are the mole fractions of A and B, respectively (see Equation 0.11). Because $x < 1$, it follows that $\ln x < 0$ and that the right-hand side of Equation 8.36 is a positive quantity, which is consistent with the spontaneous nature of the process. Because the individual ideal gas molecules do not interact, the **entropy of mixing** depends only upon the number of moles of each type of gas involved and not on the molecular identity of the two gases.

To calculate the **Gibbs free energy of mixing**, we use Equation 8.29 to give

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

Because there are no interactions between the molecules and the pressure is unchanged by the mixing process, the change in the enthalpy due to mixing, ΔH_{mix} , will be zero. Therefore,

$$\Delta G_{\text{mix}} = -T\Delta S_{\text{mix}}$$

$$\Delta G_{\text{mix}} = RT(n_A \ln x_A + n_B \ln x_B) \tag{8.37}$$

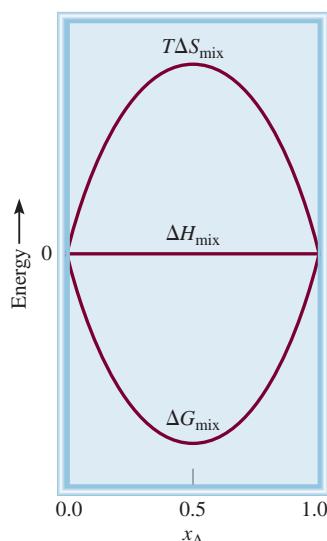


Figure 8.12 Plots of $T\Delta S_{\text{mix}}$, ΔH_{mix} , and ΔG_{mix} as functions of composition x_A for an ideal solution.

Because the right-hand side of Equation 8.37 is negative, the mixing of two ideal gases leads to a *decrease* in the Gibbs free energy. This has important consequences for the thermodynamics of chemical equilibrium, as discussed in Chapter 10. Both equations 8.36 and 8.37 can also be used to approximate the entropy and Gibbs free energy changes associated with the mixing of liquids if the interactions among the A and B molecules in the mixture are nearly equal (that is, if ΔH_{mix} is small). An idealized mixture, gas or liquid, for which $\Delta H_{\text{mix}} = 0$ and ΔG_{mix} is given by Equation 8.42 is referred to as an **ideal solution**.

Figure 8.12 shows the plots of ΔG_{mix} , ΔH_{mix} , and $T\Delta S_{\text{mix}}$ for the ideal gas mixture in Figure 8.11 as a function of composition. Both the maximum in $T\Delta S_{\text{mix}}$ and the minimum in ΔG_{mix} occur at $x_A = 0.5$. The shape of the ΔG_{mix} curve has important implications for the purification of mixtures. Suppose one sets out to separate component A from a mixture that is initially a 50:50 mixture of A and B, that is, we wish to increase the mole fraction of A in the solution. The curve for ΔG_{mix} as a function of mole fraction is relatively flat for equimolar mixtures ($x_A \approx 0.5$). Therefore, the initial steps of the purification (say from $x_A = 0.5$ to $x_A = 0.6$) require relatively little work (ΔG is small). However, as x_A approaches 1, the ΔG_{mix} curve becomes quite steep and the amount of work required to further purify the mixture becomes quite substantial (large ΔG). For this reason, obtaining very high purity in separations is often prohibitively difficult.

Example 8.12

Calculate the Gibbs free energy and entropy due to mixing 2.5 moles of argon with 3.5 moles of oxygen, both at 1 bar and 25°C. Assume ideal gas behavior.

Strategy First calculate the mole fractions of argon and oxygen, and then use them in Equation 8.36 to calculate the entropy of mixing. Next, use the calculated value of ΔS_{mix} and the relationship $\Delta G_{\text{mix}} = -T\Delta S_{\text{mix}}$ to obtain ΔG_{mix} . (Remember $\Delta H_{\text{mix}} = 0$ for an ideal solution.)

Solution The mole fractions of argon and oxygen are

$$x_{\text{Ar}} = \frac{2.5 \text{ mol}}{2.5 \text{ mol} + 3.5 \text{ mol}} = 0.42 \quad x_{\text{O}_2} = \frac{3.5 \text{ mol}}{2.5 \text{ mol} + 3.5 \text{ mol}} = 0.58$$

From Equation 8.36 (with A = Ar and B = O₂),

$$\begin{aligned} \Delta S_{\text{mix}} &= -R(n_{\text{Ar}} \ln x_{\text{Ar}} + n_{\text{O}_2} \ln x_{\text{O}_2}) \\ &= -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})[(2.5 \text{ mol}) \ln 0.42 + (3.5 \text{ mol}) \ln 0.58] \\ &= 40 \text{ J K}^{-1} \end{aligned}$$

Because $\Delta G_{\text{mix}} = -T\Delta S_{\text{mix}}$, we have

$$\begin{aligned} \Delta G_{\text{mix}} &= -T\Delta S_{\text{mix}} \\ &= -(298 \text{ K})(40 \text{ J K}^{-1}) \\ &= -1.2 \times 10^4 \text{ J} \\ &= -12 \text{ kJ} \end{aligned}$$

Check Our results correctly predict that entropy of mixing is positive and the Gibbs free energy of mixing is negative. Also, the calculated mole fractions (0.42 and 0.58) sum to 1, as required.

Practice Exercise Calculate the Gibbs free energy and entropy of mixing when 10 g of CO₂ is mixed with 20 g of O₂, both at 1.5 bar pressure and 400°C. Assume ideal behavior.

8.6 In Living Systems, Spontaneous Reactions Are Used to Drive Other Nonspontaneous, but Essential, Biochemical Processes

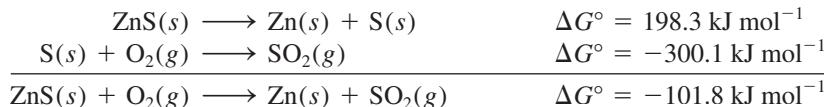
Many biochemical reactions have a positive ΔG° value, yet they still need to occur because they are essential to the maintenance of life. In living systems, these unfavorable reactions are coupled to energetically favorable processes, ones that have negative ΔG° values. The principle of ***coupled reactions*** is based on a simple concept: We can use a thermodynamically favorable reaction to drive an unfavorable one. Consider an industrial process. Suppose, for example, that we want to extract zinc from the ore sphalerite (ZnS). The following reaction will not work because it has a large positive ΔG° value:



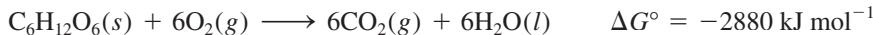
On the other hand, the combustion of sulfur to form sulfur dioxide is favored because of its large negative ΔG° value:



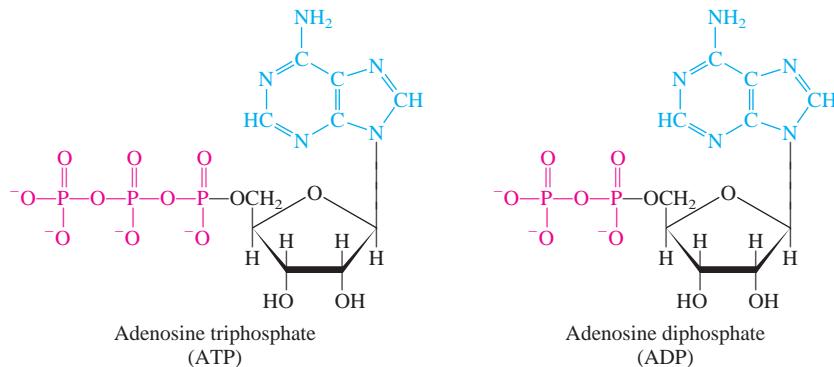
By coupling these two processes we can separate zinc from zinc sulfide. In practice, this means heating ZnS in air so that the tendency of S to form SO_2 will promote the decomposition of ZnS :



Coupled reactions play a crucial role in our survival. In biological systems, enzymes facilitate a wide variety of nonspontaneous reactions. In the human body, for example, food molecules, represented by glucose ($C_6H_{12}O_6$), are converted to carbon dioxide and water during metabolism with a substantial release of free energy:



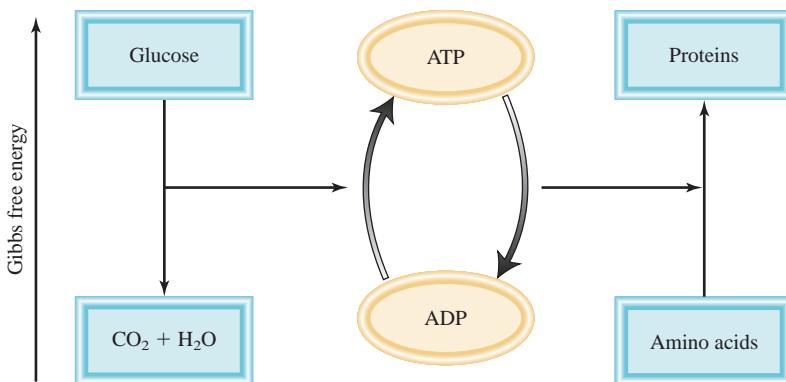
In a living cell, this reaction does not take place in a single step (as burning glucose in a flame would); rather, the glucose molecules are broken down with the aid of enzymes in a series of steps. Much of the free energy released along the way is used to synthesize adenosine triphosphate (ATP) from adenosine diphosphate (ADP) and phosphoric acid (Figure 8.13):



A mechanical analog for coupled reactions. We can make the smaller weight move upward (a nonspontaneous process) by coupling it with the falling of a larger weight.

Figure 8.13 Structures of ATP and ADP in their ionized forms. The adenine group is in blue, the ribose group in black, and the phosphate group in red. ADP has one fewer phosphate group than ATP.

Figure 8.14 A schematic representation of ATP synthesis and coupled reactions in living systems. The conversion of glucose to carbon dioxide and water during metabolism releases free energy. The released free energy is used to convert ADP into ATP. The ATP molecules are then used as an energy source to drive unfavorable reactions, such as protein synthesis from amino acids.



The function of ATP is to store free energy until it is needed by cells. Under appropriate conditions, ATP is hydrolyzed to give ADP and phosphoric acid, with a release of 31 kJ mol^{-1} of free energy, which can be used to drive energetically unfavorable reactions, such as protein synthesis.

Proteins are polymers made of amino acids. The stepwise synthesis of a protein molecule involves the joining of individual amino acids. Consider, for example, the formation of the dipeptide (a two-amino-acid unit) alanylglutamine from alanine and glycine. This reaction represents the first step in the synthesis of a protein molecule:



This reaction does not favor the formation of product, so only a little of the dipeptide would be formed at equilibrium. With the aid of an enzyme, however, the reaction is coupled to the hydrolysis of ATP as follows:



The overall free-energy change is given by $G^\circ = -31 \text{ kJ mol}^{-1} + 29 \text{ kJ mol}^{-1} = -2 \text{ kJ mol}^{-1}$, which means that the coupled reaction now favors the formation of product, and an appreciable amount of alanylglutamine will be formed under this condition. Figure 8.14 shows the ATP-ADP interconversions where energy is stored (from metabolism) and free energy is released (from ATP hydrolysis) to drive essential reactions.

Summary of Facts and Concepts

Section 8.1

- Entropy is an extensive state function that measures the number of ways that the macroscopic state of a system can be realized microscopically. Any spontaneous process must lead to a net increase in entropy in the universe (second law of thermodynamics).

Section 8.2

- Changes in entropy for a process can be defined thermodynamically in terms of the reversible work absorbed during the process.
- The thermodynamic definition of entropy can be used to calculate changes in entropy on expansion or contraction, heating or cooling, or as a result of a phase change.

Section 8.3

- The third law of thermodynamics states that the entropy of a system in its thermodynamically most stable form is zero at 0 K. The thermodynamically most stable form for most substances at 0 K is a perfect crystal. The third law enables us to measure the absolute entropies of substances.
- The standard entropy of a chemical reaction can be calculated from the absolute entropies of reactants and products.

Section 8.4

- Under conditions of constant temperature and pressure, the Gibbs free-energy change ΔG is less than zero for a

spontaneous process and greater than zero for a nonspontaneous process. For an equilibrium process, $\Delta G = 0$.

- ▶ For a chemical or physical process at constant temperature and pressure, $\Delta G = \Delta H - T\Delta S$. This equation can be used to predict the spontaneity of a process in which the initial and final states are at the same temperature and pressure.
- ▶ The standard Gibbs free-energy change for a reaction, ΔG° , can be calculated from the standard Gibbs free energies of formation of reactants and products.

Key Words

Clausius
inequality, p. 433
coupled reactions, p. 459
entropy, p. 428
entropy of mixing, p. 457
Gibbs free energy, p. 447

Gibbs free energy of
mixing, p. 457
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standard entropy change of
reaction, p. 443
standard Gibbs free energy of
formation, p. 449

standard Gibbs free energy of
reaction, p. 449
standard molar entropy, p. 441
third law of
thermodynamics, p. 440

Problems

The Entropy of an Isolated System Always Increases in Any Spontaneous Process

- 8.1 Determine the probability that all the molecules of a gas will be found in one half of a container when the gas consists of (a) 3 molecules, (b) 6 molecules, (c) 60 molecules, and (d) 2 million molecules.
- 8.2 Comment on the statement: “Even thinking about entropy increases its value in the universe.”
- 8.3 When rolling four dice, consider the microstates as corresponding to the individual numbers on each die and the macrostates as corresponding to the sum of these numbers. (a) How many microstates and macrostates are they? (b) What are the most probable and least probable macrostates. (c) What is the ratio of the number of microstates corresponding to the most probable macrostate versus the least probable macrostate.
- 8.4 Consider 12 balls placed randomly in 3 different compartments. Consider the macrostate to correspond to the number of balls in each compartment. Show that the most probable macrostate corresponds to four balls in each compartment. What is the least probable macrostate(s)?
- 8.5 According to the second law of thermodynamics, the entropy of an irreversible process in an isolated system must always increase. The entropy of living systems, however, remains small. (For example, the synthesis of highly complex protein molecules from individual amino acids is a process that leads to a

decrease in entropy.) Is the second law invalid for living systems? Explain.

The Entropy Change for a Process Can Be Calculated Using the Thermodynamic Definition of Entropy

- 8.6 Suppose that your friend told you of the following extraordinary event. A block of metal with a mass of 500 g was seen rising spontaneously from the table on which it was resting to a height of 1.00 cm above the table. She stated that the metal had absorbed thermal energy from the table that was then used to raise itself against the acceleration of gravity. (a) Does this process violate the first law of thermodynamics? (b) Does it violate the second law? Assume that the room temperature was 298 K and that the table was large enough that its temperature was unaffected by this transfer of energy. (*Hint:* First calculate the decrease in entropy as a result of this process, and then estimate the probability for the occurrence of such a process. The acceleration due to gravity is 9.81 m s^{-2} .)
- 8.7 A refrigerator is contained within a small well-insulated room and receives power from a wall socket. If the door to the refrigerator is left open, does the temperature in the room decrease, increase, or stay the same? Explain your answer.
- 8.8 The molar heat of vaporization of ethanol is 39.3 kJ mol^{-1} , and the boiling point of ethanol is 78.3°C .

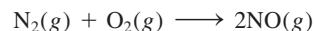
Section 8.5

- ▶ The entropy change for the mixing of two ideal gases can be calculated in terms of the mole fractions of each component. The enthalpy of mixing for two ideal gases is identically zero. Any solution that has the same formula for entropy change and enthalpy change on mixing is called an ideal solution.

Section 8.6

- ▶ Many biological reactions are nonspontaneous. They are driven by the hydrolysis of ATP, for which ΔG° is negative.

- Calculate the value of ΔS_{vap} for the vaporization of 0.50 mole of ethanol.
- 8.9 Use the thermodynamic definition of entropy and the second law to explain why heat cannot flow spontaneously from a region of low temperature to one of higher temperature.
- 8.10 Calculate the value of ΔS in heating 3.5 moles of a monatomic ideal gas from 50°C to 77°C at constant pressure.
- 8.11 Repeat the calculation in Problem 8.10 for constant-volume heating. Which one results in the greater entropy change? Give a physical explanation for the difference.
- 8.12 One mole of an ideal gas is first heated at constant pressure from T to $3T$ and then it is cooled back to T at constant volume. (a) Determine an expression for ΔS for the overall process. (b) Show that the overall process is equivalent to an isothermal expansion of the gas at T from V to $3V$, where V is the original volume. (c) Show that the value of ΔS for the process in part (a) is the same as that for part (b).
- 8.13 A sample of 1.00 g of Ne gas initially at 20°C is expanded from 1.2 to 2.6 L and simultaneously heated to 40°C. Calculate the entropy change for the process.
- 8.14 One mole of an ideal gas at 298 K expands isothermally from 1.0 to 2.0 L (a) reversibly and (b) against a constant external pressure of 12.2 bar. Calculate ΔS_{sys} , ΔS_{surr} , and ΔS_{univ} in both cases. Are your results consistent with the nature of the process?
- 8.15 The entropy of vaporization for HF is considerably smaller than the $88 \text{ J mol}^{-1} \text{ K}^{-1}$ predicted by Trouton's rule. Give a physical explanation for this exception to the rule.
- 8.16 The enthalpy of vaporization of CCl_4 at its normal boiling point of 77.6°C is $32.54 \text{ kJ mol}^{-1}$. Determine the entropy of vaporization at this temperature.
- 8.20 Explain why the value of S° for graphite is greater than that for diamond at 298 K (see Appendix 2). Would this inequality hold at 0 K?
- 8.21 Using the data in Appendix 2, calculate the standard entropy changes for the following reactions at 25°C:
- $\text{S}(s) + \text{O}_2(g) \longrightarrow \text{SO}_2(g)$
 - $\text{MgCO}_3(s) \longrightarrow \text{MgO}(s) + \text{CO}_2(g)$
- 8.22 Using the data in Appendix 2, calculate the standard entropy changes for the following reactions at 25°C:
- $\text{H}_2(g) + \text{CuO}(s) \longrightarrow \text{Cu}(s) + \text{H}_2\text{O}(g)$
 - $2\text{Al}(s) + 3\text{ZnO}(s) \longrightarrow \text{Al}_2\text{O}_3(s) + 3\text{Zn}(s)$
 - $\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l)$
- 8.23 Without consulting Appendix 2, predict whether the standard entropy change is positive or negative for each of the following reactions. Give reasons for your predictions.
- $2\text{KClO}_4(s) \longrightarrow 2\text{KClO}_3(s) + \text{O}_2(g)$
 - $\text{H}_2\text{O}(g) \longrightarrow \text{H}_2\text{O}(l)$
 - $2\text{Na}(s) + 2\text{H}_2\text{O}(l) \longrightarrow 2\text{NaOH}(aq) + \text{H}_2(g)$
 - $\text{N}_2(g) \longrightarrow 2\text{N}(g)$
- 8.24 Without consulting Appendix 2, predict whether the standard entropy change is positive or negative for each of the following reactions. Give reasons for your predictions.
- $4\text{Fe}(s) + 3\text{O}_2(g) \longrightarrow 2\text{Fe}_2\text{O}_3(s)$
 - $2\text{O}(g) \longrightarrow \text{O}_2(g)$
 - $\text{NH}_4\text{Cl}(s) \longrightarrow \text{NH}_3(g) + \text{HCl}(g)$
 - $\text{H}_2(g) + \text{Cl}_2(g) \longrightarrow 2\text{HCl}(g)$
- 8.25 Use Appendix 2 to calculate ΔS° for the reactions in Problem 8.24.
- 8.26 Consider the reaction



Calculate ΔS° for the reaction mixture, the surroundings, and the universe at 298 K. Why is your result reassuring to the inhabitants of Earth?

- 8.27 Using the data from Appendix 2, determine the standard entropy for $\text{CO}_2(g)$ at 350 K.
- 8.28 Use the following data to determine the normal boiling point of mercury (in kelvins). What assumptions must you make to do this calculation?
- $\text{Hg}(l) \quad S^\circ = 77.4 \text{ J mol}^{-1} \text{ K}^{-1}$
 $\text{Hg}(g) \quad \Delta H_f^\circ = 60.78 \text{ kJ mol}^{-1}, S^\circ = 174.7 \text{ J mol}^{-1} \text{ K}^{-1}$
- 8.29 Using the data from Appendix 2, calculate the standard entropy change for the reaction
- $$\text{H}_2(g) + \text{Cl}_2(g) \longrightarrow 2\text{HCl}(g)$$
- at 500°C. State any assumptions that you make.

The Spontaneity of a Process at Constant Temperature and Pressure Is Governed by Gibbs Free Energy

- 8.30 Using the data from Appendix 2, calculate ΔG° for the following reactions at 25°C:
- $\text{N}_2(g) + \text{O}_2(g) \longrightarrow 2\text{NO}(g)$
 - $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$
 - $2\text{C}_2\text{H}_2(g) + 5\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 2\text{H}_2\text{O}(l)$
- 8.31 Using the data from Appendix 2, calculate ΔG° for the following reactions at 25°C:
- $2\text{Mg}(s) + \text{O}_2(g) \longrightarrow 2\text{MgO}(s)$
 - $2\text{SO}_2(g) + \text{O}_2(g) \longrightarrow 2\text{SO}_3(g)$
 - $2\text{C}_2\text{H}_6(g) + 7\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 6\text{H}_2\text{O}(l)$
- 8.32 From the given values of ΔH and ΔS , predict which of the following reactions would be spontaneous at 25°C:
- $\Delta H = 10.5 \text{ kJ mol}^{-1}$, $\Delta S = 30 \text{ J mol}^{-1} \text{ K}^{-1}$
 - $\Delta H = 1.8 \text{ kJ mol}^{-1}$, $\Delta S = 113 \text{ J mol}^{-1} \text{ K}^{-1}$
- If either of the reactions is nonspontaneous at 25°C, at what temperature might it become spontaneous? State any assumptions that you make.
- 8.33 Find the temperatures at which reactions with the following ΔH and ΔS values would become spontaneous (state any assumptions that you make):
- $\Delta H = 126 \text{ kJ mol}^{-1}$, $\Delta S = 84 \text{ J mol}^{-1} \text{ K}^{-1}$
 - $\Delta H = 11.7 \text{ kJ mol}^{-1}$, $\Delta S = 105 \text{ J mol}^{-1} \text{ K}^{-1}$
- 8.34 At one time, the domestic gas used for cooking, called “water gas,” was prepared as follows:
- $$\text{H}_2\text{O}(g) + \text{C(graphite)} \longrightarrow \text{CO}(g) + \text{H}_2(g)$$

From the thermodynamic quantities listed in Appendix 2, predict whether this reaction will occur to an appreciable extent at 298 K. If not, at what temperature will the reaction begin to occur at a noticeable level? Assume ΔH° and ΔS° are temperature independent.

- 8.35 Calculate ΔG° for the process



Is the formation of graphite from diamond favored at 25°C? If so, why is it that diamonds do not become graphite on standing?

- 8.36 Predict the signs of ΔH , ΔS , and ΔG of the system for the following processes at 1 bar: (a) ammonia melts at 60°C, (b) ammonia melts at 77.7°C, (c) ammonia melts at 100°C. (The normal melting point of ammonia is 77.7°C.)
- 8.37 Ammonium nitrate (NH_4NO_3) dissolves spontaneously and endothermically in water. What can you deduce about the sign of ΔS for the solution process?

- 8.38 Using data from Appendix 2, calculate the standard Gibbs free energy of formation for $\text{NO}_2(g)$ at 400 K by (a) assuming that standard enthalpy and entropy changes are independent of temperature, and (b) by assuming that standard enthalpy and entropy changes depend on temperature but that constant-pressure heat capacities are independent of temperature.
- 8.39 Calculate ΔG° for the melting of water: $\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$ at -10.0°C (a) assuming that the enthalpy and entropy of fusion are constant over the temperature range and (b) assuming that the heat capacities are constant over the temperature range, but that the enthalpy and entropy of fusion are not.

The Mixing of Pure Substances Leads to an Increase in the Entropy and a Decrease in the Gibbs Free Energy

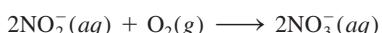
- 8.40 Calculate the changes in entropy and Gibbs free energy for the following processes: (a) the mixing of 1.00 mole of nitrogen and 1 mole of oxygen, and (b) the mixing of 3.00 moles of argon, 1 mole of helium, and 3.00 moles of hydrogen. Both parts (a) and (b) are carried out under conditions of constant temperature (298 K) and constant pressure. Assume ideal behavior.
- 8.41 At 25°C and 1 bar pressure, the absolute third-law entropies of methane and ethane are 186.19 and 229.49 $\text{J mol}^{-1} \text{ K}^{-1}$, respectively, in the gas phase. Calculate the total absolute third-law entropy of a gaseous mixture containing 1 mole of each gas. Assume ideal behavior.
- 8.42 What is the Gibbs free energy change for a process in which a mixture of 1 mole of argon gas and 1 mole of nitrogen gas is separated into two containers, each with a volume equal to half the original—one containing a mixture of 0.3 mole of argon and 0.7 mole of nitrogen, and the other containing the remainder? Repeat the calculation with 0.001 mol Ar and 0.999 mol nitrogen in the first container. Assume ideal behavior and a constant temperature of 298 K for this problem.

In Living Systems, Spontaneous Reactions Are Used to Drive Other Nonspontaneous, but Essential, Biochemical Processes

- 8.43 In the metabolism of glucose, the first step is the conversion of glucose to glucose 6-phosphate:
- $$\text{glucose} + \text{H}_3\text{PO}_4 \longrightarrow \text{glucose 6-phosphate} + \text{H}_2\text{O}$$
- $$\Delta G^\circ = 13.4 \text{ kJ mol}^{-1}$$

Because ΔG° is positive, this reaction does not favor the formation of products. Show how this reaction can be made to proceed by coupling it with the hydrolysis of ATP. Write an equation for the coupled reaction, and determine the overall ΔG° for the coupled process.

- 8.44 Certain bacteria in the soil obtain the necessary energy for growth by oxidizing nitrite to nitrate:



Given that the standard Gibbs free energies of formation (298 K) of $\text{NO}_2^-(aq)$ and $\text{NO}_3^-(aq)$ are -32.2 and $-111.3 \text{ kJ mol}^{-1}$, respectively, calculate the amount of Gibbs free energy released when 1 mole of $\text{NO}_2^-(aq)$ is oxidized to 1 mole of $\text{NO}_3^-(aq)$.

Additional Problems

- 8.45 Water freezes spontaneously at -5°C and 1 atm, but ice has a lower entropy than liquid water. Explain how a spontaneous process can lead to a decrease in entropy.
- 8.46 A certain reaction is known to have a ΔG° value of -122 kJ mol^{-1} . Will the reaction necessarily occur if the reactants are mixed together?
- 8.47 Entropy has sometimes been described as “time’s arrow” because it is the property that determines the forward direction of time. Explain.
- 8.48 A certain reaction is spontaneous at 72°C . If the enthalpy change for the reaction is 19 J, what is the *minimum* value of ΔS (in joules per kelvin) for the reaction?
- 8.49 Predict whether the entropy change is positive or negative for each of these reactions:
- $\text{Zn}(s) + 2\text{HCl}(aq) \longrightarrow \text{ZnCl}_2(aq) + \text{H}_2(g)$
 - $\text{O}(g) + \text{O}(g) \longrightarrow \text{O}_2(g)$
 - $\text{NH}_4\text{NO}_3(s) \longrightarrow \text{N}_2\text{O}(g) + 2\text{H}_2\text{O}(g)$
 - $2\text{H}_2\text{O}_2(l) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$
- 8.50 A student looked up the ΔG_f° , ΔH_f° , and S° values for CO_2 in Appendix 2. Plugging these values into Equation 8.35, he found that $\Delta G_f^\circ \neq \Delta H_f^\circ - TS^\circ$ at 298 K. What is wrong with his approach?
- 8.51 Consider the following reaction at 298 K:
- $$2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l) \quad \Delta H^\circ = -571.6 \text{ kJ mol}^{-1}$$
- Calculate ΔS_{sys} , ΔS_{surr} , and ΔS_{univ} for the reaction.
- 8.52 As an approximation, we can assume that proteins exist either in the native (physiologically functioning) state or the denatured state. The standard molar enthalpy and entropy of the denaturation of a certain protein are 512 kJ mol^{-1} and $1.60 \text{ kJ mol}^{-1} \text{ K}^{-1}$, respectively. Comment on the signs and magnitudes of these quantities, and calculate the temperature at which the process favors the denatured state.
- 8.53 Which of the following are not state functions: S , H , q , w , and T ?
- 8.54 Which of the following is not accompanied by an increase in the entropy of the system: (a) mixing of two gases at the same temperature and pressure, (b) mixing of ethanol and water, (c) discharging a battery, and (d) expansion of a gas followed by compression to its original temperature, pressure, and volume?
- 8.55 Hydrogenation reactions (for example, the process of converting $\text{C}=\text{C}$ bonds to $\text{C}-\text{C}$ bonds by the food industry) are facilitated by the use of a transition metal catalyst, such as Ni or Pt. The initial step is the adsorption, or binding, of hydrogen gas onto the metal surface. Predict the signs of ΔH , ΔS , and ΔG when hydrogen gas is absorbed onto the surface of Ni metal.
- 8.56 Calculate the entropy change for the following process: 10.0 g of oxygen (O_2) gas at a pressure of 1.0 bar and 25°C is combined in a 30.0-L container with 20.0 g of nitrogen (N_2) gas initially at a pressure of 2.0 bar and 50°C . The resulting mixture is then heated at constant pressure to 100°C .
- 8.57 When an amount of ammonium nitrate is dissolved in water, the solution becomes colder. What conclusion can you draw about ΔS° for this process? Would you expect the solubility of ammonium nitrate to increase or decrease with increasing temperature?
- 8.58 A rubber band under tension will contract when heated. Explain.
- 8.59 Older thermodynamic tables used a standard pressure of 1 atm (1.01325 bar) instead of 1 bar as is currently used. For a temperature of 25°C , calculate the difference between the standard entropy of CO at the current standard of 1 bar and its value using the older standard. What fraction of the value of S° for CO does this difference represent?
- 8.60 Comment on the correctness of the analogy sometimes used to relate a student’s dormitory room becoming untidy to an increase in entropy.
- 8.61 A heat engine operates between 210°C and 35°C . Calculate the minimum amount of heat that must be withdrawn from the hot source to obtain 2000 J of work. (See the inset on page 438–439.)
- 8.62 The internal engine of a 1200-kg car is designed to run on octane (C_8H_{18}), whose enthalpy of combustion is 5510 kJ mol^{-1} . If the car is moving up a slope, calculate the maximum height (in meters) to which the car can be driven on 1.0 gal of fuel. Assume that the engine cylinder temperature is 2200°C and that the exit temperature is 760°C , and neglect all forms of friction. The mass of 1 gallon of fuel is 3.1 kg. [Hint: The work done in moving the car over a vertical distance is mgh , where m is the mass of the car in kilograms, g is the acceleration due to gravity (9.8 m s^{-2}), and h is the height in meters.] (See the inset on pp. 438–439.)

where α is a constant that depends upon the material and T is the absolute temperature in kelvin. This equation is often used to estimate the heat capacity and standard entropy for materials at temperatures below liquid helium temperatures (4 K).

- (a) Use this equation to show that the standard entropy for a crystalline material at very low temperatures is given by

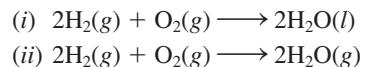
$$S^\circ = \frac{\alpha}{3}T^3$$

- (b) In an experiment, the \bar{C}_P for NaCl is measured at 12.0 K to be $0.1016 \text{ J mol}^{-1} \text{ K}^{-1}$. Use this data and the given equation for \bar{C}_P to determine the value of α for NaCl.
 (c) Using your results from parts (a) and (b), determine the standard molar entropy of NaCl at 1.0 K, 5.0 K, and 12.0 K.

Answers to Practice Exercises

- 8.1** 9.134 J K^{-1} **8.2** (a) $\Delta S < 0$, (b) $\Delta S < 0$, (c) $\Delta S > 0$, (d) $\Delta S > 0$ **8.3** -16.3 J K^{-1} **8.4** 4.31 J K^{-1} **8.5** 135 J K^{-1}
8.6 (a) $-172.84 \text{ J mol}^{-1} \text{ K}^{-1}$, (b) $-137.49 \text{ J mol}^{-1} \text{ K}^{-1}$, (c) $215.54 \text{ J mol}^{-1} \text{ K}^{-1}$ **8.7** (a) $\Delta S > 0$, (b) $\Delta S < 0$, (c) $\Delta S \approx 0$ **8.8** $-176.6 \text{ J mol}^{-1} \text{ K}^{-1}$ **8.9** (a) $-106.4 \text{ kJ mol}^{-1}$,

- 8.65** (a) Using the data in Appendix 2, calculate the standard entropy changes (ΔS°) for the following two reactions at 25°C and 80°C:



- (b) Do the ΔS° values for reactions (i) and (ii) change in the same way when temperature is increased? If not, give a physical explanation for the differences.

- 8.66** Which of the three laws of thermodynamics cannot be understood without quantum mechanics? Explain.

- 8.67** The standard enthalpy of formation and the standard entropy of gaseous benzene are $82.93 \text{ kJ mol}^{-1}$ and $269.2 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. Calculate ΔH° , ΔS° , and ΔG° for the following process at 25°C. Comment on your answers.



- (b) $-2936 \text{ kJ mol}^{-1}$ **8.10** at 25°C: $\Delta G^\circ = 117.1 \text{ kJ mol}^{-1}$; at 800°C: $\Delta G^\circ = -50.2 \text{ kJ mol}^{-1}$; at $T = 840 \text{ K}$, $\Delta G^\circ = 0$ **8.11** $-146.4 \text{ J mol}^{-1}$, $-146.5 \text{ J mol}^{-1}$, 0.07% **8.12** $\Delta S_{\text{mix}} = 5.35 \text{ J K}^{-1}$, $\Delta G_{\text{mix}} = 3.60 \text{ kJ}$

9

Chapter

Physical Equilibrium

- 9.1** The Phase Boundaries in Pure Substances Can Be Predicted Using Thermodynamics 467
- 9.2** The Solubility of a Substance Is Determined by Temperature, Pressure, and Intermolecular Forces 473
- 9.3** The Liquid-Vapor Phase Equilibrium of a Solution Can Be Understood in Terms of the Entropy of Mixing and Intermolecular Forces 483
- 9.4** Colligative Properties Are Properties of Solution Phase Equilibria That Depend Only upon the Number of Solute Molecules, Not Their Type 491



The physical state of a substance (whether it is a solid, liquid, or gas) can have a profound effect on its chemical properties. In Chapter 5, we examined the general properties of gases, liquids and solids. In this chapter, we focus on the factors that influence the transformations of a substance from one phase of matter to another. While phase transformations in pure systems are examined in Section 9.1, the remainder of the chapter deals with physical changes in solutions.

9.1 | The Phase Boundaries in Pure Substances Can Be Predicted Using Thermodynamics

In designing and implementing any chemical process, it is important to know the physical phase (solid, liquid, or gas) of each of the reactants and products under the conditions of interest (pressure, temperature, etc.). For example, the design of an industrial chemical reactor is very different for reactions in which all reactants and products are present in the same phase (*homogeneous reactions*) than for those in which at least one reactant or product is in a different phase than the others (*heterogeneous reactions*). To keep track of phase behavior, we introduced the phase diagram in Chapter 5. Recall that a phase diagram is a plot summarizing the temperature, pressure, and composition at which the various phases of a material can exist.

Figure 9.1 shows a typical phase diagram for a pure (one-component) substance. The three phase boundary lines (liquid-solid, liquid-gas, and solid-gas) meet at the triple point (the one temperature and pressure where all three phases coexist). The liquid-gas boundary line terminates at the critical point. These phase boundaries indicate how the coexistence pressure between two phases changes as the temperature changes. In this section, we will examine how we can use thermodynamics to predict the shape of phase coexistence curves for pure substances. For mixtures, more complicated phase diagrams can be constructed that indicate the dependence of the coexistence pressure and temperature upon the composition of the various phases. Phase diagrams for mixtures are discussed in Sections 9.2 and 9.3.

Two (or more) phases can be in physical equilibrium with one another only if they have the same temperature and pressure. In addition, the Gibbs free energies per mole, $\bar{G} = G/n$, of the coexisting phases at the phase boundary must also be equal. Therefore, any point of coexistence between two phases (phase α and phase β)

$$\Delta\bar{G} = \bar{G}(\text{phase } \alpha) - \bar{G}(\text{phase } \beta) = 0$$

Using this restriction and the thermodynamic concepts developed in Chapters 7 and 8, we can predict the shape of the phase boundaries.

The Clapeyron Equation

Consider points 1 and 2 along the boundary line separating phases α and β in Figure 9.2.

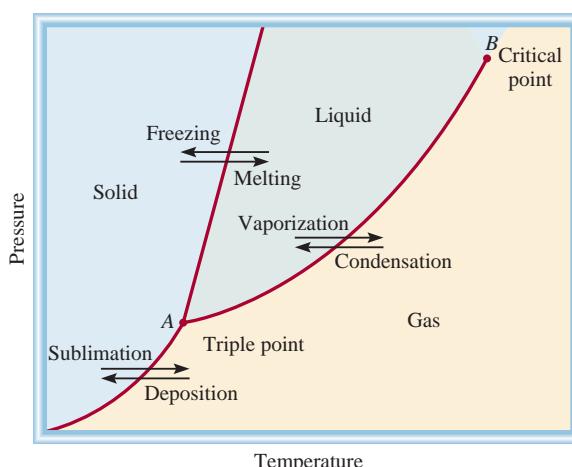
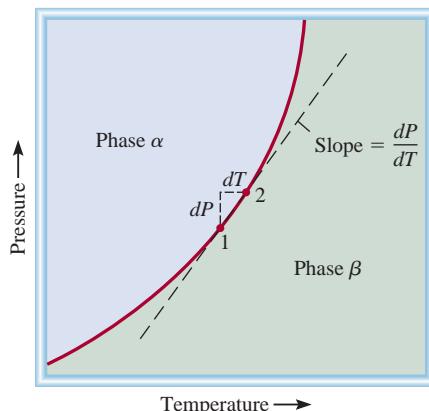


Figure 9.1 Phase diagram for a typical pure substance showing the liquid-gas, solid-liquid, and solid-gas phase coexistence boundaries. Point A where these three coexistence lines meet is the triple point. Point B at which the liquid-gas coexistence line terminates is the critical point.

Figure 9.2 The phase coexistence line between two phases, α and β . At any point along the coexistence line (e.g., point 1 or point 2), the Gibbs free energies of the two phases must be equal. This condition makes it possible to determine the slope, dP/dT , of the coexistence line from the thermodynamic properties of the two phases.



Because the phases α and β are in equilibrium, their Gibbs free energies must be equal at both points 1 and 2, that is, $G_\alpha(1) = G_\beta(1)$ and $G_\alpha(2) = G_\beta(2)$. As a result, the slope, dP/dT , of the P - T coexistence curve must be such that the change in the Gibbs free energy of phase α from point 1 to point 2 equals the corresponding change in the Gibbs free energy for phase β , that is,

$$G_\alpha(2) - G_\alpha(1) = G_\beta(2) - G_\beta(1) \quad (9.1)$$

A thermodynamic analysis of the pressure and temperature dependence of the Gibbs free energy shows that for Equation 9.1 to be satisfied, the slope, dP/dT , must obey Equation 9.2,

$$\left(\frac{dP}{dT}\right)_{\text{coex}} = \frac{\Delta S}{\Delta V} \quad (9.2)$$

where ΔS and ΔV are, respectively, the molar entropy and molar volume changes for the α to β transition, respectively: $\Delta S = S_\beta - S_\alpha$ and $\Delta V = V_\beta - V_\alpha$. Because $\Delta G = \Delta H - T\Delta S = 0$ across the phase coexistence line, we have $\Delta H = T\Delta S$, which means Equation 9.2 can be rewritten as

$$\left(\frac{dP}{dT}\right)_{\text{coex}} = \frac{\Delta H}{T\Delta V} \quad (9.3)$$

This is the **Clapeyron¹ equation**. This compact expression makes it possible to predict the change in the coexistence pressure for a given change in coexistence temperature in terms of the easily measurable thermodynamic quantities ΔH and ΔV . Equation 9.3 is a general equation governing phase coexistence and can be applied to fusion, vaporization, and sublimation, as well as to solid-solid phase transitions, such as the conversion of diamond and graphite or the fcc-to-bcc transition in iron.

The form of Equation 9.3 has important implications for melting transitions. The enthalpy of fusion is a positive quantity for all substances (i.e., heat must be added to melt all substances), but the volume change for melting can be either

1. Benoit Paul Emile Clapeyron (1799–1864). French engineer. Clapeyron made contributions to the thermodynamics of steam engines.

positive or negative depending upon whether the substance expands ($\Delta V_{\text{fus}} > 0$) or contracts ($\Delta V_{\text{fus}} < 0$) on melting. The vast majority of substances expand on melting ($\Delta V_{\text{fus}} > 0$), so the liquid is less dense than the solid. For these systems, both ΔV_{fus} and ΔH_{fus} are positive, and based on Equation 9.3, the slope of the solid-liquid coexistence curve will therefore be positive, as well. The solid-liquid coexistence curve for carbon dioxide (Figure 5.8) has a positive slope. Because dP/dT is positive, a liquid below the coexistence curve can be frozen by increasing the pressure at constant temperature.

A small number of materials contract when they melt ($\Delta V_{\text{fus}} < 0$), so the liquid is denser than the solid phase. Examples include water, gallium, antimony, bismuth, and many important semiconductors, such as silicon, germanium and gallium arsenide. (Anyone who has accidentally left a closed bottle of water in the freezer has experienced this effect!) For these systems, the slope of the solid-liquid P - T coexistence curve is negative, as seen in the phase diagram of water [Figure 5.5(a)]. In these systems, a solid state lying below the solid-liquid coexistence line melts if the pressure is increased sufficiently.

The volume changes that accompany melting are generally small (usually only a few percent). Because ΔV_{fus} is in the denominator of Equation 9.3, a small value for ΔV_{fus} means that the P - T slope of the phase boundary is large. That is, large changes in pressure are required to cause even small changes in melting temperature. Also, because both ΔV_{fus} and ΔH_{fus} do not change significantly with either temperature or pressure, the slope of the melting curve is nearly constant and the solid-liquid boundary is very close to a straight line, as seen in Figure 5.5(a).

Example 9.1 shows how to use the Clapeyron equation to determine the melting point of water at high pressure.

Example 9.1

Determine the melting temperature of pure water at 500-bar pressure. The molar volume of ice and liquid water at 273 K and 1 atm pressure are 0.0196 and 0.0180 L mol⁻¹, respectively.

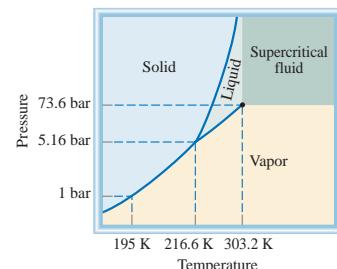
Strategy The normal melting temperature of ice at 1 atm (1.01325 bar) is 273.15 K. To find the melting temperature at 500-bar pressure, we need to find the slope of the P - T curve using the Clapeyron equation (Equation 9.3). To do this, we need both ΔV_{fus} and ΔH_{fus} . We are given the molar volumes of ice and water from which we can determine ΔV_{fus} . The value of ΔH_{fus} for water is listed in Table 7.8 ($\Delta H_{\text{fus}} = 6.01 \text{ kJ mol}^{-1}$). We can assume that the P - T melting curve is a straight line (constant slope).

Solution The Clapeyron equation, applied to fusion (melting), is

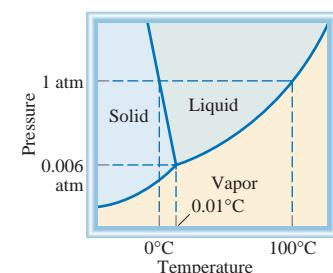
$$\left(\frac{dP}{dT}\right)_{\text{fusion}} = \frac{\Delta H_{\text{fus}}}{T\Delta V_{\text{fus}}}$$

From the given data the change in molar volume on fusion is

$$\begin{aligned}\Delta V_{\text{fus}} &= V_{\text{liquid}} - V_{\text{solid}} \\ &= 0.0180 \text{ L mol}^{-1} - 0.0196 \text{ L mol}^{-1} \\ &= -0.0016 \text{ L mol}^{-1}\end{aligned}$$



Phase diagram of carbon dioxide (Figure 5.8)



Low pressure phase diagram of water [Fig. 5.5(a)]

—Continued

Continued—

Thus,

$$\begin{aligned}\left(\frac{dP}{dT}\right)_{\text{fusion}} &\approx \frac{\Delta P}{\Delta T} = \frac{6010 \text{ J mol}^{-1}}{(273.15 \text{ K})(-0.0016 \text{ L mol}^{-1})} \\ &= -1.38 \times 10^4 \text{ J L}^{-1} \text{ K}^{-1}\end{aligned}$$

To convert to pressure units, use the conversion $1 \text{ L bar} = 100 \text{ J}$:

$$\begin{aligned}\frac{\Delta P}{\Delta T} &= -(1.38 \times 10^4 \text{ J L}^{-1} \text{ K}^{-1}) \times \frac{1 \text{ L bar}}{100 \text{ J}} \\ &= -138 \text{ bar K}^{-1}\end{aligned}$$

Thus, an increase in pressure of 138 bar is required to lower the melting point of water by 1 K.

The change in the melting point in going from 1 atm to 500 bar can then be calculated as follows:

$$\begin{aligned}\Delta T &= \frac{\Delta P}{-138 \text{ bar K}^{-1}} \\ &= \frac{500 \text{ bar} - 1.01 \text{ bar}}{-138 \text{ bar K}^{-1}} \\ &= -3.6 \text{ K}\end{aligned}$$

Thus, the new melting point is $T_m = 273.15 \text{ K} - 3.6 \text{ K} = 269.5 \text{ K}$ (or -3.6°C).

Comment The lowering of the melting point of water at high pressure is sometimes used to explain why ice-skating is possible. When the ice under the skates melts due to the pressure, a film of water is formed that then acts as a lubricant. The pressure exerted by a human on skates, however, is only on the order of 500 bar—the same as in this problem. Therefore, if pressure-induced melting were the sole mechanism lubricating the ice, it would be impossible to ice skate in temperatures below about -4°C (the melting point of ice pressurized by a human skater). It is possible to skate below -4°C , however, so other processes must be operating here. More detailed studies indicate that the main causes of lubrication in skating are ice premelting (a natural formation of a thin film of water at the surface of the ice) and melting due to frictional heating as the skates slide across the ice.

Practice Exercise What is the melting point of mercury at 500-bar pressure? The densities of liquid and solid mercury at its normal melting point (-38.9°C) are 13.69 g mL^{-1} and 14.38 g mL^{-1} , respectively. The heat of fusion for Hg is 9.75 kJ mol^{-1} .

The Clausius-Clapeyron Equation

For phase transition, such as vaporization or sublimation, in which one phase is a gas, the Clapeyron equation can be expressed in a simple approximate form. For such transitions, the molar volume of the gas phase (V_g) is so much greater than that of the liquid or solid ($V_{\text{liquid or solid}}$) that we can ignore the molar volume of the dense phase in determining the molar volume change for the transition. For example, for the molar volume change on vaporization, we can write

$$\Delta V_{\text{vap}} = V_g - V_{\text{liquid or solid}} \approx V_g$$

If the pressures are not too large, we can assume ideal gas behavior, giving

$$\Delta V_{\text{vap}} \approx V_g = \frac{RT}{P}$$

Substituting this value of ΔV_{vap} into Equation 9.3 (applied to vaporization) gives

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{T\Delta V_{\text{vap}}} \approx \frac{P\Delta H_{\text{vap}}}{RT^2}$$

where ΔH_{vap} is the molar enthalpy of vaporization (Section 7.6). After rearrangement, we have

$$\frac{dP}{P} = \frac{\Delta H_{\text{vap}}}{RT^2} dT$$

Integrating both sides from the initial pressure and temperature (P_1 and T_1) to the final state (P_2 and T_2) gives

$$\int_{P_1}^{P_2} \frac{dP}{P} = \int_{T_1}^{T_2} \frac{\Delta H_{\text{vap}}}{RT^2} dT$$

$$\ln \frac{P_2}{P_1} \approx \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (9.4)$$

where we have made the additional approximation that ΔH_{vap} is independent of T . Equation 9.4, which describes the temperature dependence of vapor pressure, is known as the **Clausius-Clapeyron equation**. As written here, Equation 9.4 applies to the vaporization of a liquid. For applications to sublimation, the enthalpy of vaporization must be replaced by ΔH_{sub} , the enthalpy of sublimation. Because the enthalpy of vaporization (or sublimation) is a positive quantity, Equation 9.4 shows that the vapor pressure of a liquid or solid increases with increasing temperature.

Example 9.2 shows how to use Equation 9.4 to determine the temperature dependence of the vapor pressure of a liquid.

Example 9.2

Diethyl ether is a volatile, highly flammable organic liquid that is used mainly as a solvent. The vapor pressure of diethyl ether is 401 mmHg at 18°C. Calculate the vapor pressure at 32°C.

Strategy We are given the vapor pressure ($P_1 = 401 \text{ mmHg}$) at a given temperature ($T_1 = 18^\circ\text{C} = 291.15 \text{ K}$). We are asked to find the vapor pressure (P_2) at a different temperature ($T_2 = 32^\circ\text{C} = 305.15 \text{ K}$). To use the Clausius-Clapeyron equation, we need to know the molar enthalpy of vaporization of diethyl ether. This value is listed in Table 7.7 ($\Delta H_{\text{vap}} = 26.0 \text{ kJ mol}^{-1}$). (The values of the molar enthalpies of vaporization given in Table 7.7 are taken at the normal boiling point, which for diethyl ether is 34.6°C. We can use this value in Equation 9.4 because we derived this equation making the assumption that ΔH_{vap} is independent of temperature over the temperature range of interest.)

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Solution Substituting these values into Equation 9.4 gives

$$\begin{aligned}\ln \frac{P_2}{P_1} &\approx \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ \ln \frac{P_2}{401 \text{ mmHg}} &\approx \frac{26,000 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{291 \text{ K}} - \frac{1}{305 \text{ K}} \right) \\ \ln \frac{P_2}{401 \text{ mmHg}} &\approx 0.493\end{aligned}$$

Taking the exponential of both sides gives

$$\begin{aligned}P_2 &= (401 \text{ mmHg}) \times e^{0.493} \\ P_2 &= 656 \text{ mmHg}\end{aligned}$$

Check The answer is reasonable because the vapor pressure should be greater at the higher temperature.

Practice Exercise The vapor pressure of ethanol is 100 mm Hg at 34.9°C. What is its vapor pressure at 63.5°C?

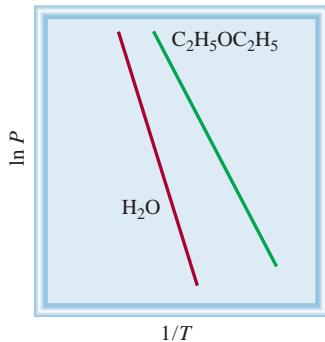


Figure 9.3 Plots of $\ln P$ versus $1/T$ for water and diethyl ether. The slopes for both graphs are equal to $-\Delta H_{\text{vap}}/R$.

When P_1 and T_1 are known, the Clausius-Clapeyron equation (Equation 9.4) has the form

$$\ln P = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} \right) + \text{constant} \quad (9.5)$$

which has the form of a straight line ($y = mx + b$). Therefore, a plot of $\ln P$ versus $1/T$ (assuming that ΔH_{vap} is independent of T) will give a straight line whose slope is equal to $-\Delta H_{\text{vap}}/R$. This method can be used to determine the heat of vaporization for a substance. Figure 9.3 shows plots of $\ln P$ versus $1/T$ for water and diethyl ether. Both are straight lines, but the one for water has a steeper slope because water has a larger ΔH_{vap} .

Example 9.3 shows how to determine the molar enthalpy of vaporization from data for the vapor pressure of a substance as a function of temperature.

Example 9.3

An experiment to determine the vapor pressure of water at a variety of temperatures between 15°C and 80°C yields the following data:

| T (°C) | 15.0 | 25.0 | 37.0 | 60.0 | 80.0 |
|-------------|-------|-------|-------|-------|-------|
| P (mm Hg) | 12.79 | 23.76 | 47.07 | 149.4 | 355.1 |

Use these data to determine the molar enthalpy of vaporization of water.

Strategy According to Equation 9.5, a plot of $\ln P$ versus $1/T$ yields a straight line whose slope is equal to $-\Delta H_{\text{vap}}/R$. The temperature data are given in degrees Celsius, so they must first be converted to absolute temperature values (in kelvins) before inverting and plotting. Also, the pressure data must be converted to $\ln P$ data.

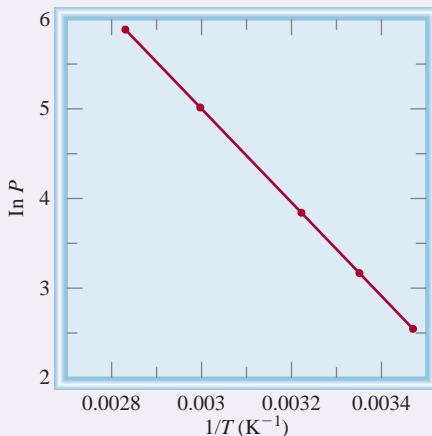
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Solution To use Equation 9.5, we must first convert the data into a suitable form for plotting:

| | | | | | |
|-------------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| $1/T \text{ (K}^{-1}\text{)}$ | 3.470×10^{-3} | 3.354×10^{-3} | 3.224×10^{-3} | 3.002×10^{-3} | 2.832×10^{-3} |
| $\ln P$ | 2.549 | 3.168 | 3.852 | 5.006 | 5.872 |

We can then plot $\ln P$ versus $1/T$, which gives a straight line.



Using a graphing calculator or computer spreadsheet computer program, least-squares linear regression (Appendix 1) gives a slope of $-5.21 \times 10^3 \text{ K}$. Thus,

$$\begin{aligned}-\Delta H_{\text{vap}}/R &= -5210 \text{ K} \\ \Delta H_{\text{vap}} &= -(8.314 \text{ J mol K}^{-1})(-5.21 \times 10^3 \text{ K}) \\ &= 43.3 \text{ kJ mol}^{-1}\end{aligned}$$

Comment This estimate of the molar heat of vaporization of water is somewhat lower than the value measured at the normal boiling point (100°C) listed in Table 7.7 ($40.79 \text{ kJ mol}^{-1}$). This apparent discrepancy arises because ΔH_{vap} is temperature dependent, so the value determined graphically in this exercise actually represents an average over the temperature interval 15°C to 80°C .

Practice Exercise The vapor pressure of mercury at various temperatures has been determined as follows:

| | | | | | |
|--------------------|--------|--------|--------|-------|-------|
| $T \text{ (K)}$ | 323 | 353 | 393.5 | 413 | 433 |
| $P \text{ (mmHg)}$ | 0.0127 | 0.0888 | 0.7457 | 1.845 | 4.189 |

Calculate the value of $\overline{\Delta H}_{\text{vap}}$ for mercury.

9.2 | The Solubility of a Substance Is Determined by Temperature, Pressure, and Intermolecular Forces

The discussion in Section 9.1 focused on phase equilibrium in pure substances. Most chemical reactions take place, though, not between pure solids, liquids, or gases, but among ions and molecules dissolved in water or other solvents. In Sections 9.2 to 9.4,

Table 9.1 Types of Solutions

| Component 1 | Component 2 | State of Resulting Solution | Examples |
|-------------|-------------|-----------------------------|---|
| Gas | Gas | Gas | Air |
| Gas | Liquid | Liquid | Soda water (CO_2 in water) |
| Gas | Solid | Solid | H_2 gas in palladium |
| Liquid | Liquid | Liquid | Ethanol in water |
| Liquid | Solid | Solid | Dental Amalgam (Hg/Ag and other metals) |
| Solid | Liquid | Liquid | NaCl in water |
| Solid | Solid | Solid | Brass (Cu/Zn), Solder (Sn/Pb) |

we examine the properties of solutions, concentrating mainly on the role of intermolecular forces in solubility and other physical properties of solutions.

Recall from Section 0.1 that a solution is a homogeneous mixture of two or more substances. Because this definition places no restrictions on the nature of the substances involved, we can identify six types of solutions, depending on the original states (solid, liquid, or gas) of the solution components. Table 9.1 lists all six types and cites examples of each. Our focus in this chapter will be on solutions involving at least one liquid component, that is, gas-liquid, liquid-liquid, and solid-liquid solutions. And, in most cases, the liquid solvent will be water.

Solutions can be characterized in terms of their capacity to dissolve a solute. A **saturated solution** contains the maximum amount of a solute that will dissolve in a given solvent at a specific temperature. This maximum solute concentration is referred to as the **solubility** of the solute in the given solvent. An **unsaturated solution** contains less solute than it has the capacity to dissolve. A third type, a **supersaturated solution**, contains more solute than is present in a saturated solution. Supersaturated solutions are unstable. In time, some of the solute will come out of a supersaturated solution as crystals.

Crystallization is the process in which dissolved solute comes out of solution and forms crystals (Figure 9.4). Both precipitation and crystallization describe the separation of an excess solid substance from a supersaturated solution. However, solids

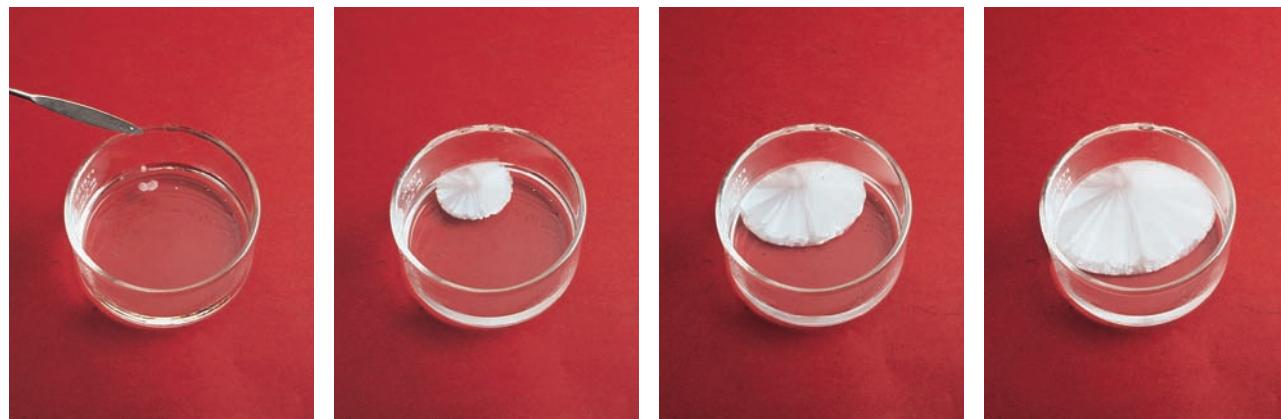


Figure 9.4 Sodium acetate crystals rapidly form in a supersaturated solution when a small seed crystal is added (left).

formed by the two processes differ in appearance. Precipitates are usually made up of small particles, whereas crystals may be large and well formed.

Chemists qualitatively refer to substances as soluble, slightly soluble, or insoluble. A substance is said to be soluble in a given solvent if an observable amount of it dissolves when added to that solvent. If not, the substance is described as slightly soluble or insoluble in the given solvent. As a general rule of thumb, a substance that has a solubility less than about 0.1 mol L^{-1} can be considered to be insoluble.

A Molecular View of the Solution Process

The intermolecular attractions that hold molecules together in liquids and solids also play a central role in the formation of solutions. When one substance (the solute) dissolves in another (the solvent), particles of the solute disperse throughout the solvent. The solute particles occupy positions that are normally taken by solvent molecules. The ease with which a solute particle replaces a solvent molecule depends on the relative strengths of three types of interactions:

- ▶ Solvent-solvent interactions
- ▶ Solute-solute interactions
- ▶ Solvent-solute interactions

Although the exact mechanism of the solution process can be complex, for the purposes of calculating the enthalpy changes associated with the dissolution process, we can imagine this process as taking place in the three distinct steps shown in Figure 9.5. (We can use any path to calculate enthalpy changes in a system because enthalpy is a state function.) The solvent molecules separate in step 1, and the solute molecules separate in step 2. (Although the solute is shown here as a crystalline solid, it could also be a liquid or gas.) These steps require an input of energy to break the attractive intermolecular forces, so they are endothermic. In step 3, the solvent and solute molecules mix. This process can be exothermic or endothermic. The heat of solution (ΔH_{soln}) is given by

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

If the solute-solvent attraction (ΔH_3) is stronger than the solvent-solvent attraction (ΔH_1) and the solute-solute attraction (ΔH_2), the solution process is favorable, or exothermic ($\Delta H_{\text{soln}} < 0$).

If the solute-solvent interaction is weaker than the solvent-solvent and solute-solute interactions, then the solution process is endothermic ($\Delta H_{\text{soln}} > 0$).

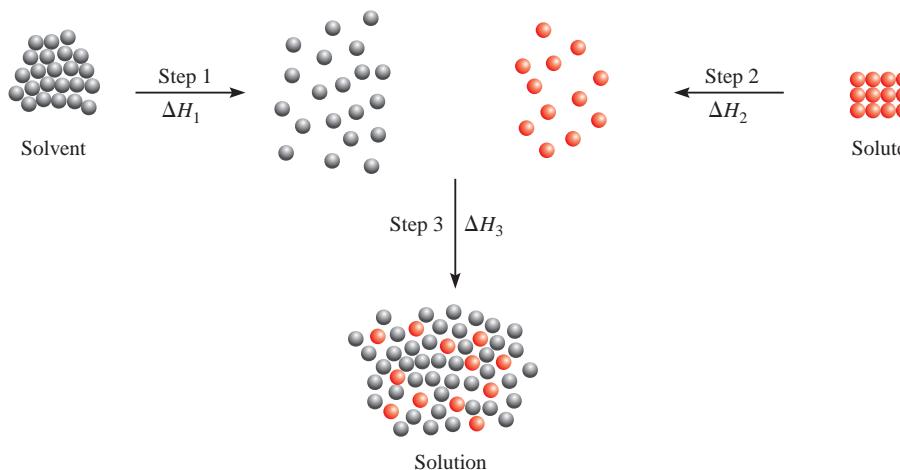
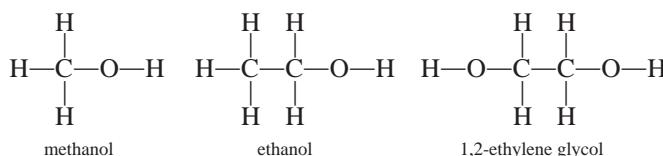


Figure 9.5 A molecular view of the solution process portrayed as taking place in three steps: First the solvent and solute molecules are separated (steps 1 and 2), and then the solvent and solute molecules mix (step 3).

Why would a solute dissolve in a solvent at all if the attraction for its own molecules is stronger than the solute-solvent attraction? The solution process, like all physical and chemical processes, is governed by an enthalpy factor and an entropy factor. The enthalpy of solution (ΔH_{sol}) determines whether a solution process is exothermic or endothermic. The entropy of solution (ΔS_{soln}), which is related to the entropy of mixing discussed in Section 8.6, generally favors dissolution, so a solute may have significant solubility in a solvent even if the solution process is endothermic.

The concept “like dissolves like” can be helpful in predicting the solubility of a substance in a given solvent. What this expression means is that two substances with intermolecular forces of similar type and magnitude are likely to be soluble in each other. For example, both carbon tetrachloride (CCl_4) and benzene (C_6H_6) are nonpolar liquids. The only intermolecular forces present in these substances are the dispersion forces discussed in Section 4.6. When these two liquids are mixed, they readily dissolve in each other, because the $\text{CCl}_4\text{-C}_6\text{H}_6$ attractions are comparable in magnitude to the $\text{CCl}_4\text{-CCl}_4$ forces and to the $\text{C}_6\text{H}_6\text{-C}_6\text{H}_6$ forces.

When two liquids are *completely soluble in each other in all proportions* they are said to be **miscible**. Although CCl_4 and C_6H_6 are miscible in each other, neither is miscible (or even soluble) in water, which is a strongly polar solvent. Acetone and alcohols such as methanol, ethanol, and 1,2-ethylene glycol are miscible with water because they can form hydrogen bonds with water molecules:



Polar substances, which dissolve easily in water, are often referred to as **hydrophilic** (*water loving*), whereas nonpolar substances that are insoluble in water are referred to as **hydrophobic** (*water fearing*).

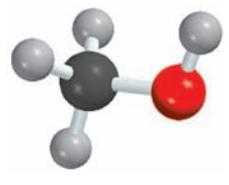
In general, ionic compounds (e.g., NaCl) are much more soluble in polar solvents, such as water, liquid ammonia, and liquid hydrogen fluoride, than in nonpolar solvents, such as benzene and carbon tetrachloride. Because the molecules of nonpolar solvents lack a dipole moment, they cannot effectively solvate cations (e.g., Na^+) and anions (e.g., Cl^-). (**Solvation** is the process in which an ion or a molecule is surrounded by solvent molecules arranged in a specific manner. The process is called **hydration** when the solvent is water.) The predominant intermolecular interaction between ions and nonpolar compounds is an ion-induced dipole interaction, which is much weaker than an ion-dipole interaction (see Section 4.6). Consequently, ionic compounds usually have extremely low solubilities in nonpolar solvents. (The qualitative and quantitative prediction of the solubility of specific ionic compounds in water is discussed in Chapter 10.)

Example 9.4 shows how to qualitatively predict solubility based on the intermolecular forces in the solute and the solvent.

Example 9.4

Predict the relative solubilities in the following cases: (a) bromine (Br_2) in benzene (C_6H_6 , $\mu = 0 \text{ D}$) and in water ($\mu = 1.87 \text{ D}$), (b) KCl in carbon tetrachloride (CCl_4 , $\mu = 0 \text{ D}$) and in liquid ammonia (NH_3 , $\mu = 1.46 \text{ D}$), and (c) formaldehyde (CH_2O) in carbon disulfide (CS_2 , $\mu = 0$) and in water.

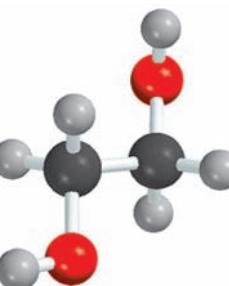
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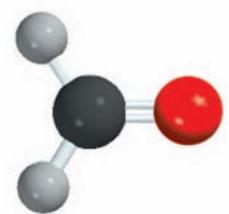
CH_3OH
(methanol)



$\text{C}_2\text{H}_5\text{OH}$
(ethanol)



$\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$
(1,2-ethylene glycol)



CH_2O
(formaldehyde)

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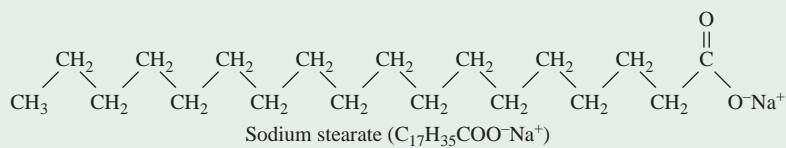
Strategy To predict the solubility of a particular compound in a particular solvent, remember that like dissolves like. Thus, a nonpolar solute will dissolve in a nonpolar solvent; ionic compounds will generally dissolve in polar solvents due to favorable ion-dipole interaction; and solutes that can form hydrogen bonds with the solvent will be very soluble in the solvent.

- Solution** (a) Br_2 is a nonpolar molecule, so it should be more soluble in C_6H_6 (also nonpolar) than in water (very polar). The only intermolecular forces between Br_2 and C_6H_6 are dispersion forces.
- (b) KCl is an ionic compound. For it to dissolve, the individual K^+ and Cl^- ions must be stabilized by ion-dipole interactions. Because CCl_4 has no dipole moment, KCl should be more soluble in liquid NH_3 , a polar molecule with a large dipole moment.
- (c) Because CH_2O is a polar molecule and CS_2 (a linear molecule) is nonpolar, the forces between molecules of CH_2O and CS_2 are weak dipole-induced dipole interactions and dispersion forces. On the other hand, CH_2O can act as a hydrogen-bond acceptor with water, so it should be more soluble in H_2O than in CS_2 .

Practice Exercise Is iodine (I_2) more soluble in water or in carbon disulfide (CS_2)?

The concept of like dissolves like helps explain how soap works to remove oily substances. Sodium stearate, a typical soap molecule, has a polar head group and a long nonpolar hydrocarbon tail that is nonpolar (Figure 9.6).

The cleansing action of soap is due to the dual nature of the soap molecule (hydrophobic tail and hydrophilic head). The hydrocarbon tail is readily soluble in oily substances, which are also nonpolar, while the ionic— COO^- group remains outside the oily surface. When enough soap molecules have surrounded an oil droplet, as shown in Figure 9.7, the entire system becomes stabilized in water because the exterior portion is now largely hydrophilic. This is how soap removes greasy substances from surfaces such as hands, dishes, and clothing.



(a)

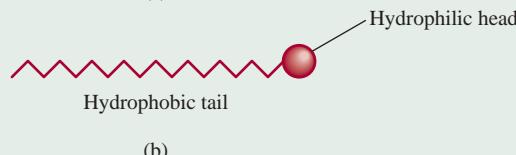
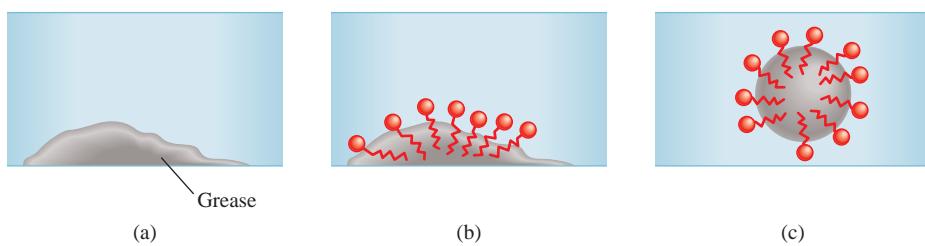


Figure 9.6 (a) A sodium stearate molecule. (b) The simplified representation of the molecule that shows a hydrophilic head and a hydrophobic tail.

Figure 9.7 The cleansing action of soap. (a) Grease (oily substance) is insoluble in water. (b) When soap is added to water, the nonpolar tails of the soap molecules dissolve in the grease, leaving the polar head groups on the surface, exposed to water. (c) The grease is removed in the form of an emulsion in which each oily droplet has an ionic exterior that is hydrophilic.



The Effect of Temperature on Solubility

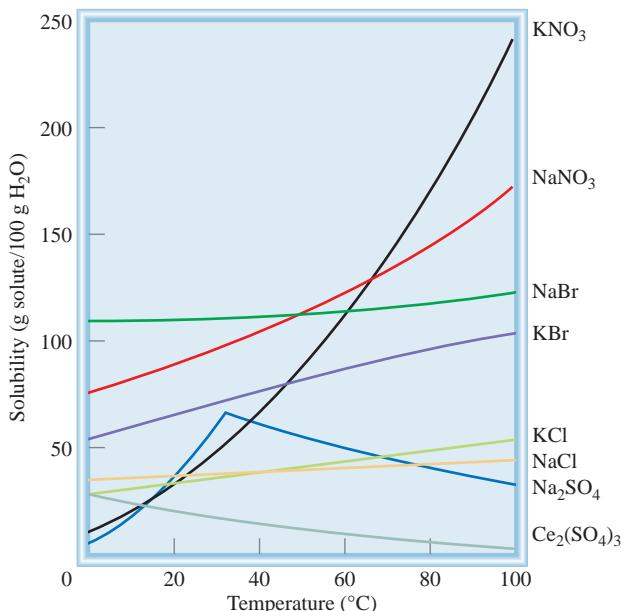
Recall that solubility is defined as the maximum amount of a solute that will dissolve in a given quantity of solvent *at a specific temperature and pressure*. Figure 9.8 shows how the solubility of some ionic compounds in water depends on the temperature. In most but certainly not all cases, the solubility of a solid substance increases with temperature.

For reasons that will be discussed in Section 10.6, the temperature dependence of the solubility can be predicted from the enthalpy change associated with adding solute to a saturated solution ΔH_{sat} . If ΔH_{sat} is positive (i.e., if the addition of solute is an endothermic process), then the solubility of the solute will *increase* with increasing temperature. If ΔH_{sat} is negative (i.e., if the addition of solute is an exothermic process), then the solubility of the solute will *decrease* with increasing temperature.

The value of ΔH_{sat} can differ from the infinite dilution enthalpy of solution ΔH_{soln} defined in Section 7.6 for two reasons:

- ▶ The enthalpy of solution at infinite dilution ΔH_{soln} is the enthalpy change associated with the addition of a solute to a *pure solvent*, whereas ΔH_{sat} is the enthalpy change associated with the addition of solute to a *saturated solution*.
- ▶ The stable form of an ionic solid at saturation is often a hydrate. The enthalpy of solution for hydrates is generally positive (endothermic), especially at

Figure 9.8 Temperature dependence of the solubility of some ionic compounds in water.



saturation. For this reason, the solubility of an ionic compound may increase with temperature, even though the ΔH_{soln} for the anhydrous form is negative (exothermic).

The infinite dilution enthalpy ΔH_{soln} for anhydrous Na_2SO_4 , for example, is -23 kJ mol^{-1} . Based on this value, the solubility of sodium sulfate should *decrease* with increasing temperature. It does at high temperatures, according to Figure 9.8, but at low temperatures the solubility *increases* with increasing temperature. This occurs because the stable form between 0°C and about 30°C is not the anhydrous compound, but the decahydrate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, for which the enthalpy of solution is positive (endothermic) at saturation. Above about 30°C , the stable solid form is anhydrous Na_2SO_4 , and the solubility decreases with temperature as predicted by the negative value of ΔH_{soln} .

The dependence of the solubility of a solid on temperature varies considerably, as shown in Figure 9.9. For example, the solubility of KNO_3 , for example, increases sharply with temperature, while the solubilities of NaBr and NaCl change very little. This wide variation makes it possible to obtain pure substances from mixtures through the process of ***fractional crystallization***, defined as *the separation of a mixture of substances into pure components on the basis of their differing solubilities*.

Suppose we have 90 g of KNO_3 that is contaminated with 10 g of NaCl . To purify the KNO_3 sample, we dissolve the mixture in 100 mL of water at 60°C and then gradually cool the solution to 0°C . At this temperature the solubilities of KNO_3 and NaCl are 12.1 g/100 g H_2O and 34.2 g/100 g H_2O , respectively. Thus, 78 g of KNO_3 (that is, 90 g $-$ 12 g) will crystallize out of the solution but all the NaCl will remain dissolved (Figure 9.9). In this manner, we can obtain about 90 percent of the original amount of KNO_3 in pure form. The KNO_3 crystals can be separated from the solution by filtration. Many of the solid inorganic and organic compounds that are used in the laboratory are purified by fractional crystallization. The method usually works best if

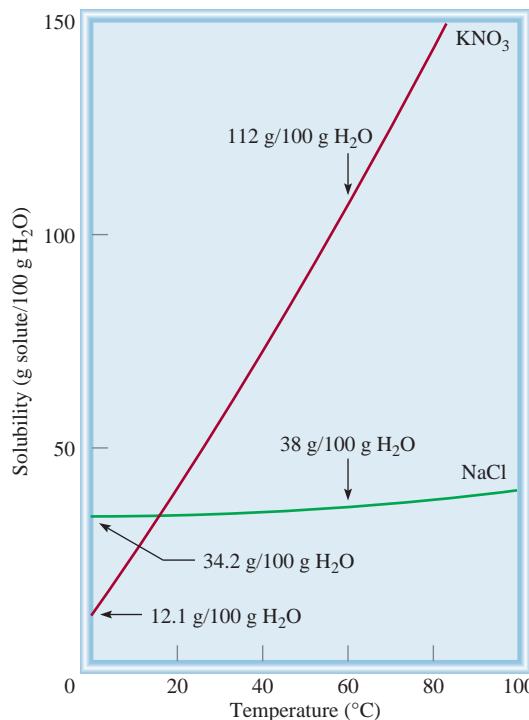


Figure 9.9 Graph of the temperature dependence of the solubilities of KNO_3 and NaCl in water. KNO_3 is considerably more soluble at high temperatures (that is, 60°C) than at low temperatures (that is, 0°C), whereas the solubility of NaCl increases only slightly as the temperature increases. The difference in temperature dependence makes it possible to isolate pure KNO_3 from a solution containing both salts via fractional crystallization.

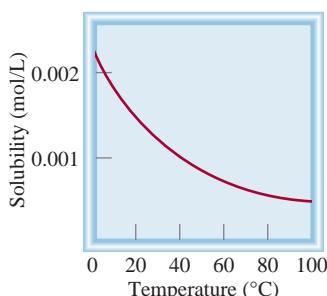


Figure 9.10 Graph of the temperature dependence of the solubility of O_2 gas in water. The solubility decreases as the temperature increases. The pressure of the gas over the solution is 1 bar.

the compound to be purified has a steep solubility curve, that is, if it is considerably more soluble at high temperatures than at low temperatures. Otherwise, much of it will remain dissolved as the solution is cooled. Fractional crystallization also works well if the amount of impurity in the solution is relatively small.

Temperature and Gas Solubility

When a gas is put in contact with a solvent, some of the gas molecules will dissolve in the liquid. This process is usually exothermic, so the solubility of gases in water usually *decreases* with increasing temperature (Figure 9.10). When water is heated in a beaker, bubbles of air form on the side of the glass before the water boils. As the temperature rises, the dissolved air molecules begin to “boil out” of the solution long before the water itself boils.

The reduced solubility of molecular oxygen in hot water contributes to the problem of *thermal pollution*, that is, the heating of the environment (usually waterways) to temperatures that are harmful to its living inhabitants. It is estimated that every year in the United States some 100,000 billion gallons of water are used for industrial cooling, mostly in electric power and nuclear power production. This process heats the water, which is then returned to the rivers and lakes from which it was taken. Fish, like all other cold-blooded animals, have much more difficulty coping with rapid temperature fluctuations in the environment than humans do. An increase in water temperature accelerates their rate of metabolism, which generally doubles with each 10°C rise. The speedup of metabolism increases the fish’s need for oxygen at the same time that the supply of oxygen is diminished because of its lower solubility in heated water.

Understanding how gas solubility varies with temperature can improve your chances of catching a fish, too. On a hot summer day, an experienced angler usually picks a deep spot in the river or lake to cast their bait. Because the oxygen content is greater in the deeper, cooler region, most fish will be found there.

The Effect of Pressure on the Solubility of Gases

For all practical purposes, external pressure has no influence on the solubilities of liquids and solids, but it greatly affects the solubility of gases. The quantitative relationship between gas solubility and pressure is given by **Henry’s² law**, which states that *the equilibrium concentration of a gas dissolved in a liquid is proportional to the pressure of the gas over the solution:*³

$$c = k_H P \quad (9.6)$$

Here c is the molar concentration (mol L^{-1}) of the dissolved gas; P is the pressure (in bar) of the gas over the solution; and k_H is the *Henry’s law constant*, which for a given gas, depends only on the temperature and the identity of the solvent. The

2. William Henry (1775–1836). English chemist. Henry’s major contribution to science was his discovery of the law describing the solubility of gases, which now bears his name.

3. In advanced studies, Henry’s law is often written as $P_i = x_i K_{H,i}$, where x_i is the mole fraction of the solute gas in the solution and P_i is the partial pressure of the gas in the vapor phase. In this form, Henry’s law constant $K_{H,i}$ has units of pressure. Equation 9.6 can be derived from this equation by noting that, for dilute solutions, the mole fraction of a solute is proportional to its concentration. In Section 9.3, we will demonstrate how this form of Henry’s law results from the vapor-liquid equilibrium of real binary liquids.

Table 9.2 Henry's Law Constants for Select Gases in Water at 298 K

| Gas | Henry's Law Constant k_H (mol L ⁻¹ bar ⁻¹) |
|--|---|
| H ₂ | 7.8×10^{-4} |
| He | 3.7×10^{-4} |
| Ne | 4.5×10^{-4} |
| Ar | 1.4×10^{-3} |
| Kr | 2.4×10^{-3} |
| Xe | 4.3×10^{-3} |
| N ₂ | 6.2×10^{-4} |
| O ₂ | 1.3×10^{-3} |
| CO ₂ | 3.4×10^{-2} |
| CH ₄ (methane) | 1.4×10^{-3} |
| C ₂ H ₆ (ethane) | 1.9×10^{-3} |
| C ₃ H ₈ (propane) | 1.4×10^{-3} |
| C ₄ H ₈ (n-butane) | 1.1×10^{-3} |

constant k_H has the units mol L⁻¹ bar⁻¹. When the pressure of the gas is 1 bar, c is numerically equal to k_H . If several gases are present, P is the partial pressure. Henry's law constants for several common gases at 298 K are listed in Table 9.2. Because the solubility of gases generally decreases with increasing temperature, the Henry's law constants also generally decrease with temperature.

A practical demonstration of Henry's law is the effervescence of a soft drink when the cap of the bottle is removed. Before the beverage bottle is sealed, it is pressurized with a mixture of air and CO₂ saturated with water vapor. Because of the high partial pressure of CO₂ in the pressurizing gas mixture, the amount dissolved in the soft drink is many times the amount that would dissolve under normal atmospheric conditions. When the cap is removed, the pressurized gases escape. Eventually the pressure in the bottle falls to atmospheric pressure, and the amount of CO₂ remaining in the beverage is determined only by the normal atmospheric partial pressure of CO₂ (0.0003 bar). The excess dissolved CO₂ comes out of solution, causing the effervescence. Example 9.5 applies Henry's law to nitrogen gas.

Example 9.5

The solubility of nitrogen gas in water at 25°C and 1 bar is 6.3×10^{-4} mol L⁻¹.

What is the concentration of nitrogen dissolved in water under atmospheric conditions?

The partial pressure of nitrogen gas in the atmosphere is 0.79 bar.

Strategy The given solubility enables us to calculate Henry's law constant (k_H), which can then be used to determine the concentration of the solution.

—Continued

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Solution The first step is to calculate k_H in Equation 9.6:

$$\begin{aligned} c &= k_H P \\ 6.3 \times 10^{-1} \text{ mol L}^{-1} &= k_H (1 \text{ bar}) \\ k_H &= 6.3 \times 10^{-4} \text{ mol L}^{-1} \text{ bar}^{-1} \end{aligned}$$

Then, plug the calculated value of k_H and the given value of P into Equation 9.6 to determine the solubility of nitrogen gas in water under normal atmospheric conditions:

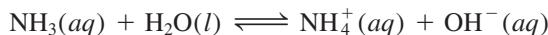
$$\begin{aligned} c &= (6.3 \times 10^{-4} \text{ mol L}^{-1} \text{ bar}^{-1})(0.79 \text{ bar}) \\ &= 5.0 \times 10^{-4} \text{ mol L}^{-1} \\ &= 5.0 \times 10^{-4} M \end{aligned}$$

The solubility of N_2 decreases because the pressure was lowered from 1 bar to 0.79 bar.

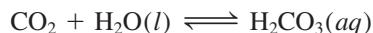
Check The ratio of the concentrations [$(5.0 \times 10^{-4} M) / (6.3 \times 10^{-4} M)$] = 0.79] should be equal to the ratio of the pressures (0.79 bar/1.0 bar = 0.79).

Practice Exercise Calculate the molar concentration of oxygen in water at 25°C for a partial pressure of 0.22 bar.

For most gases, the relationship between Henry's law and solubility is straightforward, however, in cases where the dissolved gas can undergo a reaction with the solvent, the solubility will be underestimated by Henry's law. For example, the solubility of ammonia in water is much higher than predicted by Henry's law because NH_3 reacts with H_2O :



Henry's law predicts the amount of dissolved $\text{NH}_3(aq)$ present in the solution, but the total amount of NH_3 from the gas phase that dissolves in solution is given by the sum of $\text{NH}_3(aq)$ and $\text{NH}_4^+(aq)$. Similarly, the solubility of carbon dioxide will be underestimated using Henry's law because CO_2 also reacts with water, as follows:



For such gases, the solubility requires the combined use of Henry's law and the equations governing the reaction equilibrium in solution, which will be discussed in Chapter 10.

Another important example is the dissolution of molecular oxygen in blood. Normally, oxygen gas is only sparingly soluble in water, the solvent in blood (see the Practice Exercise in Example 9.5). The solubility of O_2 in blood is significantly higher, however, because blood contains a high concentration of hemoglobin (Hb) molecules. Each hemoglobin molecule can bind up to four oxygen molecules, which are eventually delivered to the tissues for use in metabolism:



Thus, molecular oxygen is highly soluble in blood because it binds to hemoglobin.

The box text applies Henry's law to a natural disaster that occurred at Lake Nyos in Cameroon (west Africa).

The Killer Lake

Disaster struck swiftly and without warning. On August 21, 1986, Lake Nyos in Cameroon, a small nation on the west coast of Africa, suddenly belched a dense cloud of carbon dioxide. Speeding down a river valley, the cloud asphyxiated over 1700 people and many livestock.

How did this tragedy happen? Lake Nyos is stratified into layers that do not mix. A boundary separates the freshwater at the surface from the deeper, denser solution containing dissolved minerals and gases, including CO₂. The CO₂ gas comes from springs of carbonated groundwater that percolate upward into the bottom of the volcanically formed lake. Given the high water pressure at the bottom of the lake, the concentration of CO₂ gradually accumulated to a dangerously high level, in accordance with Henry's law.

What triggered the release of CO₂ is not known for certain. It is believed that an earthquake, landslide, or even strong winds may have upset the delicate balance within the lake, creating waves that overturned the water layers. When the deep water rose, dissolved CO₂ came out of solution, just as a soft drink fizzes when the bottle is uncapped. Being heavier than air, the CO₂ traveled close to the ground and literally smothered an entire village 15 miles away. Now, more than 18 years after the incident, scientists are concerned that the CO₂ concentration at the bottom of Lake Nyos is again reaching saturation level. To prevent a recurrence of the earlier tragedy, an attempt has been made to pump up the deep water, thus releasing the dissolved CO₂. In addition to being costly, this approach is controversial because it might disturb the waters near the bottom of the lake, leading to an uncontrollable release of CO₂ to the surface. In the meantime, a natural time bomb is ticking away.



Deep waters in Lake Nyos are pumped to the surface to remove dissolved CO₂ gas.

9.3 | The Liquid-Vapor Phase Equilibrium of a Solution Can Be Understood in Terms of the Entropy of Mixing and the Intermolecular Forces

Sections 9.3 and 9.4 examine phase equilibrium in mixtures, focusing primarily on systems in which at least one of the coexisting phases is a liquid solution (i.e., vapor-liquid, liquid-liquid, and solid-liquid solution phase equilibrium).

Liquid-Vapor Equilibrium of Ideal Solutions

A liquid solution that is a mixture of two components, A and B, is called a *binary liquid mixture* (or *binary solution*). Like a single-component liquid, this solution will have a vapor pressure (P) that depends upon the temperature. For a binary solution, though, the vapor pressure will also depend upon the composition of the liquid, defined by the mole fractions x_A^l and x_B^l , where the superscript "l" denotes the liquid phase. The composition of the vapor above a binary liquid mixture, denoted by x_A^v and x_B^v (v for "vapor"), will usually differ from that of the liquid.

If the vapor is considered ideal, then the total vapor pressure, described by Dalton's law, is the sum of the partial pressures of components A and B.

$$P_T = P_A + P_B \quad (9.7)$$

In the late nineteenth century, François-Marie Raoult⁴ observed that for many binary liquid mixtures, the partial pressure of component i in the equilibrium vapor phase is given by the mole fraction of the component in the solution (x_i^l) times the vapor pressure of i in its pure liquid form (P_i^*):

$$P_i = x_i^l P_i^* \quad (9.8)$$

This is known as **Raoult's law**. In Section 8.6, we defined an *ideal solution* of two liquids as one in which the enthalpy of mixing is zero and the entropy of mixing is given by Equation 8.48. It can be shown using thermodynamics that Raoult's law is exactly satisfied for ideal solutions. In fact, the converse is also true (i.e., any solution that follows Raoult's law can be shown to be ideal), so an ideal solution can be alternatively defined as any solution that follows Raoult's law.

For an ideal binary solution, the total vapor pressure (P_T) can be determined by combining Equations 9.7 and Raoult's Law (Equation 9.8):

$$P_T = x_A^l P_A^* + x_B^l P_B^* \quad (9.9)$$

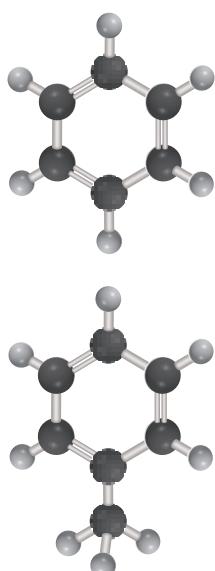
For a given value of x_A^l , however, the mole fraction of B is given by $x_B^l = 1 - x_A^l$, so Equation 9.9 can be written as

$$P_T = x_A^l P_A^* + (1 - x_A^l) P_B^*$$

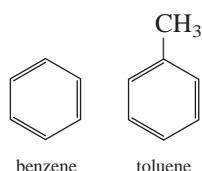
$$P_T = P_B^* + x_A^l (P_A^* - P_B^*) \quad (9.10)$$

which defines a straight line with slope $(P_A^* - P_B^*)$ and intercept P_B^* .

On the molecular level, the interactions between A and B molecules in an ideal binary solution are identical to the interactions between A molecules and the interactions between B molecules. Although no solution is strictly ideal, many come close. For example, benzene (C_6H_6) and toluene (C_7H_8) have very similar structures, and therefore very similar intermolecular interactions, and are known to form a very nearly ideal solution when mixed:



Benzene (C_6H_6) and toluene (C_7H_8).



The graph in Figure 9.11 shows how the total vapor pressure (P_T) in a benzene-toluene solution at 80.1°C depends on the composition of the solution (as expressed by the mole fraction of benzene).

As predicted by Equation 9.10 for ideal solutions, the total vapor pressure above the benzene-toluene solution as a function of the mole fraction of benzene is a straight

4. François-Marie Raoult (1830–1901). French chemist. Raoult's work was mainly in solution properties and electrochemistry.

line connecting the vapor pressure of pure toluene (at $x_{\text{benzene}}^l = 0$) and the vapor pressure of pure benzene (at $x_{\text{benzene}}^l = 1$).

Example 9.6 shows how to use Equation 9.10 to calculate the vapor pressure of an ideal solution.

Example 9.6

Benzene (C_6H_6) and toluene (C_7H_8) form a nearly ideal solution. The vapor pressures of pure benzene and pure toluene are 94.6 and 29.1 torr at 298 K, respectively.

- (a) Calculate the total vapor pressure above a solution formed by mixing 25.0 g of benzene and 25.0 g of toluene. (b) Calculate the mole fractions of benzene and toluene in the vapor phase.

Strategy Assuming that the mixture of benzene and toluene is an ideal solution, the partial pressures of both benzene and toluene can be calculated using Raoult's law (Equation 9.8). To do this we need to convert grams of both benzene and toluene to moles and then determine the mole fractions. (a) The total vapor pressure is then obtained by adding together the partial pressures of benzene and toluene. (b) The mole fractions of benzene and toluene in the vapor phase can be determined from the partial pressures using Dalton's law.

Solution The number of moles of benzene and toluene are calculated as follows:

$$\text{moles of benzene} = \frac{25.0 \text{ g benzene}}{78.1 \text{ g mol}^{-1}} = 0.320 \text{ mol}$$

$$\text{moles of toluene} = \frac{25.0 \text{ g toluene}}{92.1 \text{ g mol}^{-1}} = 0.271 \text{ mol}$$

The mole fraction of benzene (x_{benzene}^l) is then given by

$$\begin{aligned} x_{\text{benzene}}^l &= \frac{\text{moles of benzene}}{(\text{moles of benzene}) + (\text{moles of toluene})} \\ &= \frac{0.320 \text{ mol}}{0.320 \text{ mol} + 0.271 \text{ mol}} = 0.541 \end{aligned}$$

The mole fraction of toluene (x_{toluene}^l) could be calculated in a similar fashion, but it is easier to use the following relationship, which works because this is a two-component mixture: $x_{\text{benzene}}^l + x_{\text{toluene}}^l = 1$. Thus,

$$x_{\text{toluene}}^l = 1 - x_{\text{benzene}}^l = 1 - 0.541 = 0.459$$

Using Raoult's law and the vapor pressures of pure benzene and toluene, the partial pressure of each component can be calculated as follows:

$$\begin{aligned} P_{\text{benzene}} &= x_{\text{benzene}}^l P_{\text{benzene}}^* = (0.541)(94.6 \text{ torr}) = 51.2 \text{ torr} \\ P_{\text{toluene}} &= x_{\text{toluene}}^l P_{\text{toluene}}^* = (0.459)(29.1 \text{ torr}) = 13.3 \text{ torr} \end{aligned}$$

- (a) The total vapor pressure is then $P_{\text{total}} = 51.2 \text{ torr} + 13.3 \text{ torr} = 64.5 \text{ torr}$.
(b) According to Dalton's law, the partial pressure of a gas is equal to its mole fraction (x^v) times the total pressure (P_{total}), so

$$x_{\text{benzene}}^v = \frac{P_{\text{benzene}}}{P_{\text{total}}} = \frac{51.2 \text{ torr}}{64.5 \text{ torr}} = 0.794$$

$$x_{\text{toluene}}^v = 1 - x_{\text{benzene}}^v = 1 - 0.794 = 0.206$$

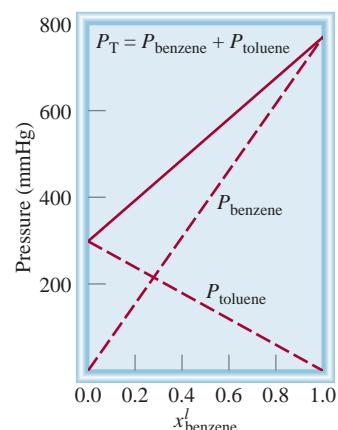


Figure 9.11 Graph of the dependence of the total and partial pressures of a benzene-toluene binary liquid mixture as functions of the mole fractions of each component ($x_{\text{toluene}} = 1 - x_{\text{benzene}}$) at 80.1°C. This solution can be considered to be nearly ideal because the vapor pressures are well approximated by Raoult's law.

—Continued

Continued—

Check Benzene has a higher vapor pressure than toluene, so the mole fraction of benzene in the vapor phase should be larger than that in the liquid phase, which is consistent with our result.

Practice Exercise Hexane (C_6H_{14}) and heptane (C_7H_{16}) form a nearly ideal solution. The vapor pressures of pure hexane and pure heptane are 151 and 46.0 torr at 298 K, respectively. (a) Calculate the total vapor pressure above a solution formed by mixing 50.0 g of hexane and 100.0 g of heptane. (b) Calculate the mole fractions of hexane and heptane in the vapor phase.

Equation 9.10 gives the total vapor pressure as a function of the composition of the liquid phase, expressed as x_A^l . We can also express the total vapor pressure as a function of the vapor composition, x_A^v . According to Dalton's law of partial pressures (Equation 5.24), the mole fraction of A in the vapor phase is

$$x_A^v = \frac{P_A}{P_T}$$

Using Raoult's law and Equation 9.10, we have

$$x_A^v = \frac{x_A^l P_A^*}{P_B^* + x_A^l (P_A^* - P_B^*)} \quad (9.11)$$

Multiplying Equation 9.11 through by the right-hand-side denominator and solving for x_A^l gives

$$x_A^l = \frac{x_A^v P_B^*}{P_A^* - x_A^v (P_A^* - P_B^*)} \quad (9.12)$$

Applying Raoult's law ($P_A = x_A^l P_A^*$) and Dalton's law ($P_A = x_A^v P_T$) to Equation 9.12 gives the total pressure as a function of the vapor composition:

$$P_T = \frac{x_A^l P_A^*}{x_A^v} = \frac{P_A^* P_B^*}{P_A^* - x_A^v (P_A^* - P_B^*)} \quad (9.13)$$

The plots of the total vapor pressure as functions of the mole fraction of A in both the liquid and vapor phases are shown in Figure 9.12(a) and (b), respectively. The combined plot shown in Figure 9.12(c) is a liquid-vapor phase diagram for an ideal binary solution at a fixed temperature T —often called a **pressure-composition diagram**. At any pressure and composition above the upper curve (the liquid line) the mixture is a liquid. Below the lower curve (the vapor line), the mixture is entirely vapor. The region between the two curves is a region of phase coexistence, that is, both liquid and vapor phases are present in the system.

The line *a-e* in Figure 9.12(c) represents what happens if we start with a liquid solution above the upper curve and slowly lower the pressure at fixed temperature and overall composition from point *a* to point *e*. The solution remains entirely liquid until point *b* where we enter the coexistence region and some of the liquid begins to evaporate to form a vapor phase. From point *b* to point *d*, the system consists of both liquid

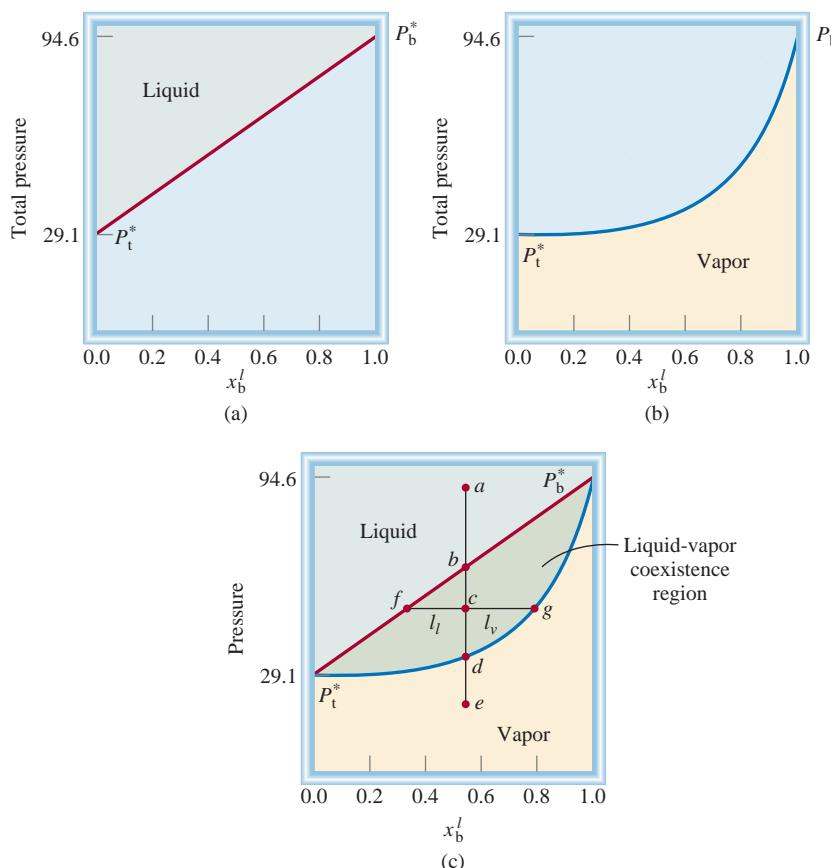


Figure 9.12 Vapor-liquid phase equilibrium in a benzene-toluene solution as a function of pressure at 23°C. (a) The total vapor pressure as a function of the mole fraction of benzene in the liquid. (b) The total vapor pressure as a function of the mole fraction of benzene in the vapor. (c) The pressure-composition phase diagram constructed by combining plots (a) and (b). The line *f-g* is the tie line corresponding to the system at point *c*.

and vapor in coexistence. At any given pressure in the coexistence region, the composition of the liquid and vapor is given by the points where a horizontal line crosses the upper and lower curves, respectively. This line is called a *tie line*. At point *c*, therefore, the system consists of a liquid with a composition given by point *f* and a vapor with a composition given by point *g*. The tie line for this system is the line *f-g* in Figure 9.12(c). The fraction of the system that is liquid or vapor can be found using the **lever rule**:

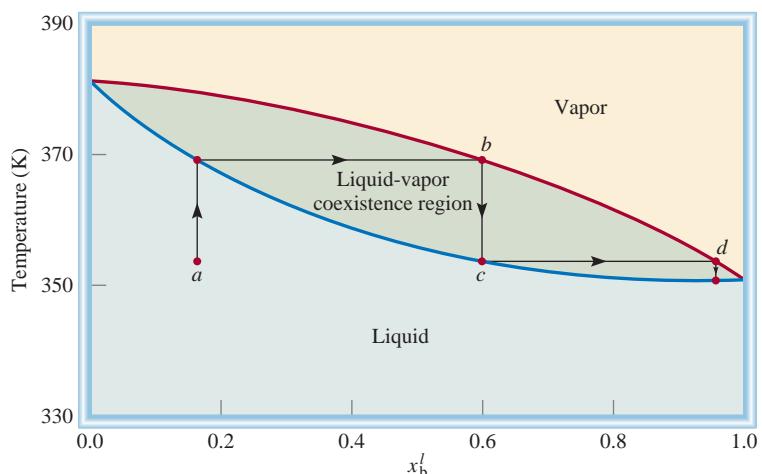
$$n_l l_l = n_v l_v \quad (9.14)$$

where n_l and n_v are the number of moles in the liquid and vapor phases, respectively, and l_l and l_v are the distances between point *c* and the upper (liquid) curve (*f-c*) and the lower (vapor) curve (*c-g*), respectively [see Figure 9.12(c)].

In constructing Figure 9.12 we have assumed that component A is the more volatile component (i.e., $P_A^* > P_B^*$). At a given total vapor pressure P , the mole fraction of A in the vapor (x_A^v) is larger than the mole fraction of A in the coexisting liquid (x_A^l). This is a general result for liquid-vapor coexistence in ideal and nearly ideal solutions—the vapor phase is richer in the more volatile component than in the liquid phase.

Another common way of representing a binary liquid-vapor equilibrium is through a **temperature-composition phase diagram**, in which the pressure is held fixed and phase coexistence is examined as a function of temperature and composition. Figure 9.13 shows the temperature-composition phase diagram for the benzene-toluene system at a pressure of 1 atm. In Figure 9.13, the lower curve (the *boiling-point curve*)

Figure 9.13 Temperature-composition phase diagram for the liquid-vapor equilibrium in benzene-toluene mixtures at 1 atm. The boiling points of toluene and benzene are 110.6°C and 80.1°C, respectively.



gives the liquid composition as a function of temperature. For temperatures and compositions below this curve, only the liquid phase is possible. Similarly, the upper curve (the *dew-point curve*) represents the vapor composition as a function of pressure. Any system with a temperature and composition above this curve will consist of vapor only. As for the pressure-composition phase diagram, the region between the two curves corresponds to systems in which liquid and vapor phases coexist.

Fractional Distillation

The temperature-composition phase diagram can be used to illustrate *fractional distillation*, a procedure for separating liquid components of a solution based on their different boiling points. Suppose we begin by heating a mixture of benzene and toluene with a temperature and composition corresponding to point *a* of Figure 9.13. When the temperature reaches about 370 K, the liquid will begin to boil. The vapor that results has a composition given by point *b*, where the tie line intersects the dew point curve. If the vapor is separated from the liquid and condensed by cooling to point *c*, the resulting liquid solution is richer in benzene than the original solution. If the condensate at point *c* is heated further, the vapor that results has the composition corresponding to point *d*. At this point the mixture is very nearly pure benzene, so this process separates benzene from the initial solution. For nearly ideal solutions such as benzene-toluene, this procedure can be repeated until the desired purity is reached.

In practice, chemists use an apparatus like that shown in Figure 9.14 to separate volatile liquids. The round-bottomed flask containing the benzene-toluene solution is fitted with a long column packed with small glass beads. When the solution boils, the vapor condenses on the beads in the lower portion of the column, and the liquid falls back into the distilling flask. As time goes on, the beads gradually heat up, allowing the vapor to move upward slowly and not condense back into the flask. In essence, the packing material causes the benzene-toluene mixture to be subjected continuously to numerous vaporization-condensation steps. At each step, the composition of the vapor in the column will be richer in the more volatile, or lower boiling-point, component (in this case, benzene). The vapor that rises to the top of the column is essentially pure benzene, which is then condensed and collected in a receiving flask.



Typical industrial fractional distillation columns in an oil refinery.

Fractional distillation is as important in industry as it is in the laboratory. The petroleum industry employs fractional distillation on a large scale to separate the components of crude oil.

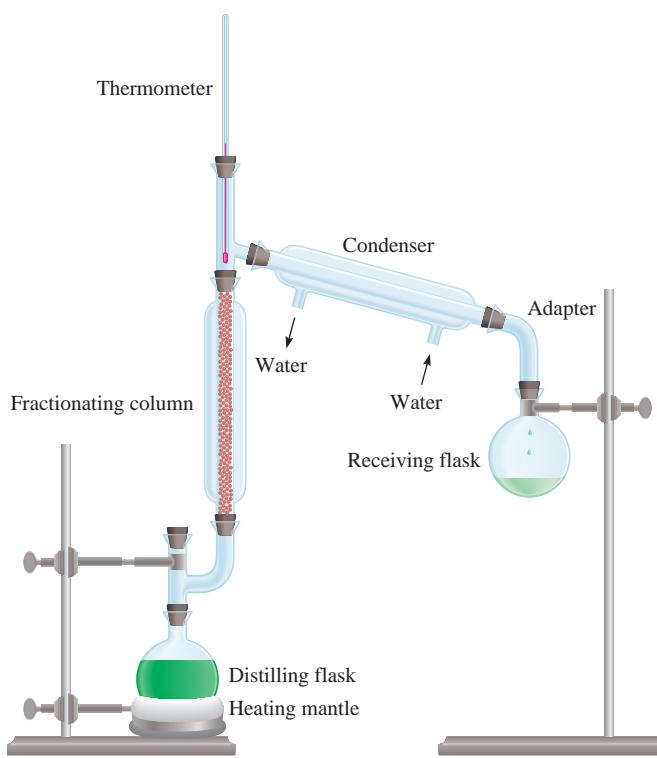


Figure 9.14 An apparatus for small-scale fractional distillation. The fractionating column is packed with tiny glass beads. The longer the fractionating column, the more complete the separation of the volatile liquids.

Vapor-Liquid Equilibrium in Nonideal Solutions

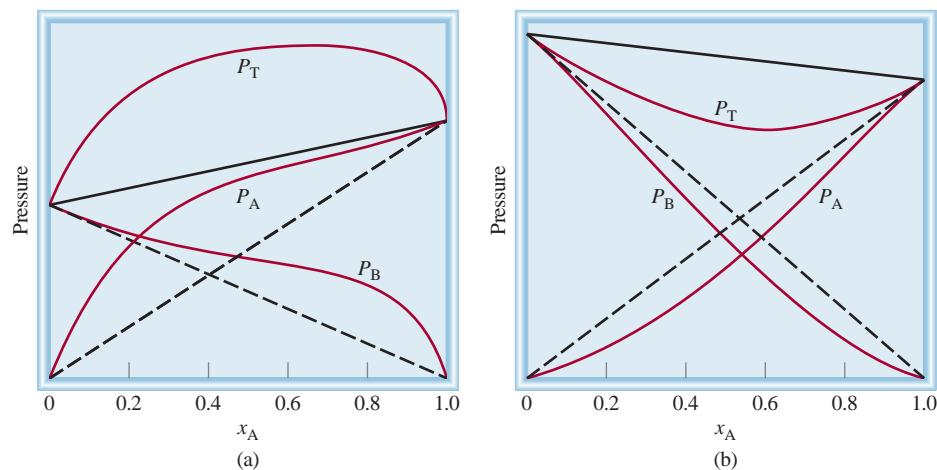
Although Raoult's law is an important starting point in understanding vapor-liquid equilibrium in solutions, most real solutions deviate from ideal behavior. The nature and magnitude of these deviations can be understood in terms of the intermolecular interactions between two volatile substances A and B. Consider the following two cases:

Case 1: If the intermolecular forces between A and B molecules are weaker than those between A molecules and those between B molecules, then there is a greater tendency for these molecules to leave the solution than in the case of an ideal solution. Consequently, the vapor pressure of the solution is greater than the sum of the vapor pressures as predicted by Raoult's law for the same concentration. This behavior gives rise to the *positive deviation* shown in Figure 9.15(a). In this case, the enthalpy of solution is positive (that is, mixing is an endothermic process). An ethanol-water solution is an example of a system with a positive deviation from Raoult's law because the hydrogen bonding interactions between ethanol molecules and water molecules are weaker than those between water molecules.

Case 2: If A molecules attract B molecules more strongly than they do their own kind, the vapor pressure of the solution will be less than the sum of the vapor pressures as predicted by Raoult's law. This gives rise to the *negative deviation* shown in Figure 9.15(b). In this case, the enthalpy of solution is negative (i.e., mixing is an exothermic process).

Binary solutions that deviate significantly from ideal behavior (as exemplified in their temperature-composition phase diagrams) have important consequences for fractional distillation processes. Figure 9.16 shows two types of such phase diagrams for

Figure 9.15 Pressure-composition curves for nonideal solutions. (a) Positive deviation occurs when P_T is greater than that predicted by Raoult's law (the solid black line). (b) Negative deviation occurs when P_T is less than that predicted by Raoult's law (the solid black line).



nonideal solutions. The phase diagram in Figure 9.16(a) is for a system that exhibits a strong *positive deviation* from Raoult's law. This system will show a *minimum boiling point*. Examples of these systems are ethanol-water, ethanol-benzene, and *n*-propanol-water. The phase diagram in Figure 9.16(b) is for a system that exhibits a strong *negative deviation* from Raoult's law, which will yield a *maximum boiling point*. These solutions, which include nitric acid-water and acetone-chloroform, are less common than those with minimum boiling points.

Both of these phase diagrams exhibit a point (at the minimum or the maximum) where the liquid and vapor curves coincide. At these points, the solutions form an *azeotrope*, which is a solution for which the liquid phase and the vapor phase have the same composition. A solution with a *low-boiling azeotrope* [Figure 9.16(a)] cannot be purified completely by distillation because the distillation process will always converge to the azeotrope, as illustrated by the fractional distillation pathways *a-d* and *e-h* in

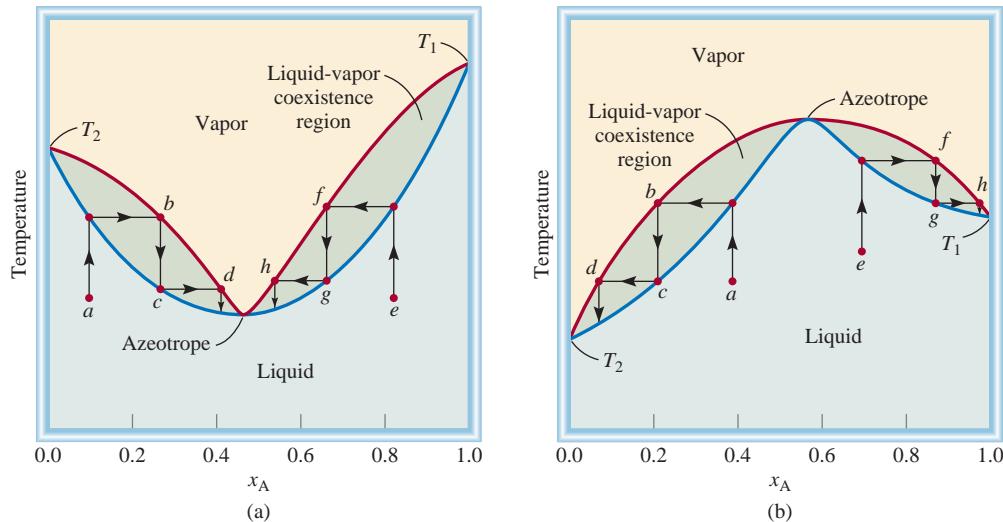


Figure 9.16 Different types of liquid-vapor phase diagrams for a binary liquid mixture of component A and B as functions of x_A , the mole fraction of the component with the higher boiling temperature. (a) The phase diagram for a system with a low-boiling azeotrope (minimum boiling point) and (b) the phase diagram for a system with a high-boiling azeotrope (maximum boiling point). The arrows show how the paths for various distillation processes depend upon the position of the initial composition relative to the azeotrope.

Figure 9.16(a). Solutions with a **high-boiling azeotrope** [Figure 9.16(b)] can be purified by distillation, but the component that is separated depends upon which side of the azeotrope the initial concentration lies. For example, following the fractional distillation pathway *a-d* in Figure 9.16(b) will eventually lead to a solution that is nearly pure component B and the pathway *e-h* will lead to nearly pure component A.

9.4 | Colligative Properties Are Properties of Solution Phase Equilibria That Depend Only upon the Number of Solute Molecules, Not Their Type

Four general properties of dilute liquid solutions are vapor-pressure lowering, boiling-point elevation, freezing-point depression, and osmotic pressure. These properties are commonly referred to as **colligative** (or **collective**) **properties** because they are bound together through their common origin—they depend *only on the number of solute molecules present in the solution, not on the nature (size, molecular mass, etc.) of the solute molecules*. For solutes that are **nonelectrolytes** (*i.e.*, they do not dissociate into ions in solution), colligative properties typically hold for concentrations less than about 0.1 *M*.

All of the colligative properties can be understood in terms of the free energy of mixing for ideal solutions. A dilute liquid solution usually behaves as an ideal solution (or approximately so), that is, the solution obeys Raoult's law and has a free energy of mixing given by Equation 8.54:

$$\Delta G_{\text{mix}} = RT(n_A \ln x_A + n_B \ln x_B)$$

Equation 8.54 can be rewritten as

$$\Delta G_{\text{mix}} = nRT(x_A \ln x_A + x_B \ln x_B) \quad (9.15)$$

where n ($= n_A + n_B$) is the total number of moles in the solution. If we let the solvent be represented by A and the solute by B, then $\Delta G_{\text{mix}} = 0$ for the pure solvent ($x_A = 1$, $x_B = 0$). If we add a small amount of solute (B) to the pure solvent to form a dilute solution, then $\Delta G_{\text{mix}} < 0$ because both the solvent and solute mole fractions (x_A and x_B) will be less than one and greater than zero and their natural logarithms will both be negative. Thus, a solution formed by adding a small amount of solute to a solvent will have a lower free energy (and thus be more stable) than the original pure solvent. Because the enthalpy of mixing, ΔH_{mix} , is zero for an ideal solution, this decrease of the free energy is due to the increase in entropy accompanying the dissolution process.

In discussing colligative properties, we shall initially make two important approximations: (1) the solutions are dilute enough that they can be considered to be ideal and (2) the solutes are nonelectrolytes. Also, for simplicity, we will only consider two-component systems (that is, systems containing a solvent and a single solute).

Vapor-Pressure Lowering

If a solute is **nonvolatile** (that is, if it *does not have a measurable vapor pressure*), the vapor pressure of its solution is always less than that of the pure solvent. Thus, the relationship between solution vapor pressure and solvent vapor pressure depends on the concentration of the solute in the solution. This phenomenon is known as **vapor-pressure lowering**. Consider a solution that contains a solvent (A) and a

nonvolatile solute (B), such as a solution of sucrose (table sugar) in water. Because the solution is ideal, Raoult's law (Equation 9.8) can be used to determine the vapor pressure of the solution:

$$P_A = x_A P_A^* \quad (9.8)$$

where P_A^* is the vapor pressure of the pure solvent. Because $x_A = 1 - x_B$, Equation 9.8 can be rewritten as

$$P_A = (1 - x_B)P_A^* \quad (9.16)$$

Rearranging Equation 9.16 gives

$$P_A^* - P_A = \Delta P = x_B P_A^* \quad (9.17)$$

where ΔP , the decrease in the vapor pressure from that of the pure solvent, is directly proportional to the mole fraction of the solute.

Why does the vapor pressure of a solvent decrease when a solute is added? It cannot be due to the modification of intermolecular forces because vapor-pressure lowering occurs even in ideal solutions, in which the solute-solvent and solvent-solvent interactions are considered to be identical. The correct explanation is based on an analysis of the Gibbs free energy of mixing. When a pure solvent is in coexistence with its vapor phase, the molar Gibbs free energies of the solvent in the vapor and liquid phases must be equal for the system to be in equilibrium. As discussed previously, adding a small amount of solute to the solvent decreases the Gibbs free energy due to the increase in entropy accompanying the dissolution process. To maintain equilibrium, the Gibbs free energy of the vapor must also decrease. Because the solute is nonvolatile and does not enter the vapor phase, there is no Gibbs free energy of mixing in the vapor. At a fixed temperature, the only way to lower the free energy of a pure vapor is to reduce its pressure (which reduces the density of solvent molecules in the vapor). Thus, the vapor pressure of the solution must decrease to maintain equilibrium as solute is added.

Example 9.7 shows how to calculate the vapor pressure of a solution of water and a nonvolatile solute.

Example 9.7

Calculate the vapor pressure of a solution made by dissolving 218 g of glucose (molar mass = 180.2 g mol⁻¹) in 460 mL of water at 30°C. What is the vapor-pressure lowering value? The vapor pressure of pure water at 30°C is 31.82 mmHg. Assume the density of the solution is 1.00 g mL⁻¹.

Strategy Use Equation 9.8 (Raoult's law) to determine the vapor pressure of the solution. Glucose is a nonvolatile solute.

Solution The vapor pressure of a solution (P_A) is given by Raoult's law:

$$P_A = x_A P_A^*$$

Because the vapor pressure of pure water (P_A^*) is given, we only need to find x_A , the mole fraction of water in the solution, to calculate P_A . To determine x_A , we must first

—Continued



C₆H₁₂O₆ (glucose)

Continued—

calculate the number of moles of glucose and the number of moles of water in the solution:

$$n_A(\text{water}) = 460 \text{ mL} \times \frac{1.00 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 25.5 \text{ mol}$$

$$n_B(\text{glucose}) = 218 \text{ g} \times \frac{1 \text{ mol}}{180.2 \text{ g}} = 1.21 \text{ mol}$$

The mole fraction of water (x_A) is given by

$$x_A = \frac{n_A}{n_A + n_B}$$

$$= \frac{25.5 \text{ mol}}{25.5 \text{ mol} + 1.21 \text{ mol}} = 0.955$$

The vapor pressure of pure water at 30°C (given in the problem statement) is 31.82 mmHg, so the vapor pressure of the glucose solution is

$$P_A = 0.955 \times 31.82 \text{ mmHg}$$

$$= 30.4 \text{ mmHg}$$

Finally, the vapor-pressure lowering is $31.82 \text{ mmHg} - 30.4 \text{ mmHg} = 1.4 \text{ mmHg}$.

Check We can also calculate the vapor-pressure lowering by using Equation 9.17 (i.e., $\Delta P = x_B P_A^*$). Because the mole fraction of glucose (x_B) is $1 - 0.955 = 0.045$, the vapor-pressure lowering is given by $(0.045)(31.82 \text{ mmHg}) = 1.4 \text{ mmHg}$.

Practice Exercise A solution is prepared by dissolving 82.4 g of urea $[(\text{NH}_2)_2\text{CO}]$ in 212 g of water at 35°C. What is the vapor pressure of this solution? What is the vapor-pressure lowering? (Urea is a nonvolatile solute.)

Boiling-Point Elevation

The normal boiling point of a solution is the temperature at which its vapor pressure equals 1 atm (see Section 5.1). When a nonvolatile solute is added to a pure solvent at its normal boiling point, its vapor pressure is lowered below 1 atm. To bring the solution back to the boiling point, we must increase the temperature until the vapor pressure of the solution is 1 atm. As a result, the boiling temperature of the solution will be higher than that of the pure solvent. This phenomenon is known as **boiling-point elevation**.

Like vapor-pressure lowering, boiling-point elevation can be understood in terms of the free energy of mixing. At 1 atm, the boiling temperature is the temperature at which the molar Gibbs free energy of the liquid phase is equal to that of the vapor phase. When a small amount of a nonvolatile solute is added to a solvent, its Gibbs free energy is lowered due to the entropy of mixing. The Gibbs free energy of the vapor phase is unaffected, however, because no solute is present. As Figure 9.17 shows, the liquid and vapor curves intersect at a higher temperature when the Gibbs free energy of the liquid phase is lowered, consistent with an increase in the boiling temperature due to mixing.

Numerically, the **boiling-point elevation** (ΔT_b) is defined as *the boiling point of the solution (T_b) minus the boiling point of the pure solvent (T_b^*)*:

$$\Delta T_b = T_b - T_b^* \quad (9.18)$$

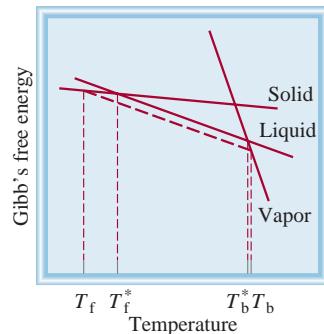


Figure 9.17 The solid red curves show the Gibbs free energies for the solid, liquid, and vapor phases of a pure solvent at 1 atm pressure, all as functions of temperature. The boiling point is given by the point of intersection of the liquid and vapor curves, and the freezing point is the point of intersection of the liquid and solid curves. The * is used to indicate values corresponding to the pure solvent. When a solute is added to the liquid phase, the Gibbs free energy of the resulting liquid solution (dotted curve) is lowered due to the entropy of mixing, causing the liquid and vapor curves to intersect at a higher temperature, that is, the boiling point is raised by the addition of the solute. In contrast, the lowering of the liquid curve causes the liquid and solid lines to intersect at a lower temperature, that is, the freezing point is lowered by the addition of the solute.

Because $T_b > T_b^*$, ΔT_b is a positive quantity. The value of ΔT_b is proportional to the vapor-pressure lowering, so it is also proportional to the mole fraction of the solute, x_B . It can be shown that, as long as the solution is dilute and the temperature change is small, the boiling-point elevation is given by

$$\Delta T_b = \frac{RT_b^2}{\Delta H_{\text{vap}}} x_B \quad (9.19)$$

where ΔH_{vap} is the enthalpy change due to vaporization. To convert the mole fraction x_B to a more practical concentration unit, such as molality (m_B), we write

$$x_B = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A} = \frac{n_B}{w_A/M_A}$$

where w_A is the mass of the solvent in kg and M_A is the molar mass of the solvent in kg mol⁻¹. Because n_B/w_A gives the molality of the solution, m_B , it follows that $x_B = M_A m_B$, so

$$\Delta T_b = \frac{RT_b^2 M_A}{\Delta H_{\text{vap}}} m_B \quad (9.20)$$

All the quantities in the first term on the right-hand side of Equation 9.20 are constants for a given solvent, so we have

$$\Delta T_b = K_b m_B \quad (9.21)$$

where K_b , the **molal boiling-point elevation constant** (or *ebullioscopic constant*), is given by

$$K_b = \frac{RT_b^2 M_A}{\Delta H_{\text{vap}}} \quad (9.22)$$

The units of K_b are K mol⁻¹ kg. The concentration portion of K_b is based on molality, not molarity, because the temperature of the system (the solution) is *not* constant. Recall from Section 0.3 that molality is independent of temperature, whereas molarity changes with temperature.

Table 9.3 lists values of K_b for several common solvents. Use the boiling-point elevation constant for water and Equation 9.21 to prove to yourself that the boiling

Table 9.3 Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids

| Solvent | Normal Freezing Point (°C)* | K_t (K kg mol ⁻¹) | Normal Boiling Point (°C)* | K_b (K kg mol ⁻¹) |
|-------------|-----------------------------|---------------------------------|----------------------------|---------------------------------|
| Water | 0 | 1.86 | 100 | 0.52 |
| Benzene | 5.5 | 5.12 | 80.1 | 2.53 |
| Ethanol | -117.3 | 1.99 | 78.4 | 1.22 |
| Acetic acid | 16.6 | 3.90 | 117.9 | 2.93 |
| Cyclohexane | 6.6 | 20.0 | 80.7 | 2.79 |

*Measured at 1 atm.

point of water will be 100.52°C if the molality of an aqueous nonelectrolyte solution is 1.00 m .

Freezing-Point Depression

Ice on frozen roads and sidewalks melts when sprinkled with salts such as NaCl or CaCl_2 . This method of thawing succeeds because it depresses the freezing point of water. As in boiling-point elevation, the Gibbs free energy of the solvent is decreased due to mixing by the addition of a small amount of solvent. The Gibbs free energy of the solid is unaffected as long as no solvent is incorporated into the crystal lattice. As a result, the temperature at which the solution Gibbs free energy curve crosses the solid free energy curve (i.e., the melting temperature) will be lower than that for the pure solvent (see Figure 9.17). The lowering of the freezing point of a solvent when a solute is added is called *freezing-point depression*.

Quantitatively, the **freezing-point depression** (ΔT_f) is defined as *the freezing point of the pure solvent (T_f^*) minus the freezing point of the solution (T_f)*:

$$\Delta T_f = T_f^* - T_f \quad (9.23)$$

Because $T_f^* > T_f$, ΔT_f is a positive quantity. Just as in boiling-point elevation, the freezing point depression for dilute solutions is proportional to the molality of the solute (m_B):

$$\Delta T_f = K_f m_B \quad (9.24)$$

where K_f , the **molal freezing-point depression constant** (or *cryoscopic constant*), is given by

$$K_f = \frac{RT_f^2 M_A}{\Delta H_{\text{fus}}} \quad (9.25)$$

In Equation 9.25, ΔH_{fus} is the molar enthalpy change of fusion for the solvent. Like K_b , K_f has the units $\text{K mol}^{-1} \text{kg}$. Values of K_f for some common solvents are listed in Table 9.3.

The phenomena of freezing-point depression and boiling-point elevation can also be understood by studying the phase diagram in Figure 9.18. At 1 atm, the normal



De-icing of airplanes is based on freezing-point depression.



In cold climate regions, antifreeze must be used in car radiators in winter.

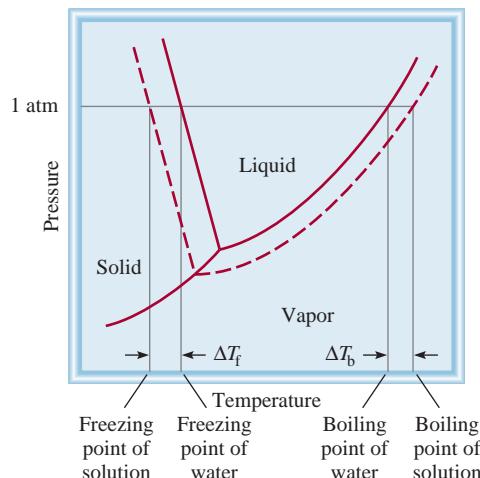
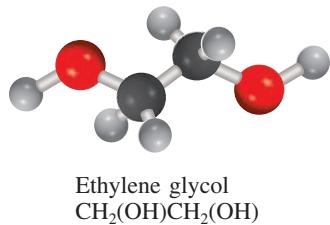


Figure 9.18 Phase diagram illustrating the boiling-point elevation and freezing-point depression of aqueous solutions. The dashed curves pertain to the solution and the solid curves to the pure solvent. The boiling point of the solution is *higher* than that of water, whereas the freezing point of the solution is *lower* than that of water.

freezing point of the solution lies at the intersection of the dashed curve (between the solid and liquid phases) and the horizontal line at 1 atm. Although the solute must be nonvolatile in the case of boiling-point elevation, no such restriction applies to freezing-point depression. Ethanol (C_2H_5OH), for example, a fairly volatile liquid that boils at only $78.5^\circ C$, is sometimes used as an antifreeze additive to lower the freezing point of water in automobile radiators.

A practical application of freezing-point depression and boiling-point elevation is described in Example 9.8.



Example 9.8

Ethylene glycol (EG) [$CH_2(OH)CH_2(OH)$] is a common automobile antifreeze. It is water soluble and fairly nonvolatile (b.p. $197^\circ C$). Calculate the freezing point of a solution containing 651 g of EG in 2505 g of water. Should you keep this substance in your car radiator during the summer? The molar mass of EG is 62.01 g.

Strategy We must use Equation 9.24 to calculate the depression in freezing point of the solution. First, though, we must calculate the molality of the solution, which we can determine from the information given in the problem statement. Refer to Table 9.3 for the value of K_f for the solvent (water).

Solution To solve for the molality of the solution, we need to know the number of moles of EG and the mass of the solvent in kilograms.

$$\text{moles of solute} = 651 \text{ g EG} \times \frac{1 \text{ mol EG}}{62.07 \text{ g EG}} = 10.5 \text{ mol EG}$$

The mass of the solvent is given in the problem statement as 2505 g. This can be converted to 2.505 kg, so the molality is calculated as follows:

$$\begin{aligned} m &= \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} \\ &= \frac{10.5 \text{ mol EG}}{2.505 \text{ kg}} = 4.19 \text{ mol kg}^{-1} \\ &= 4.19 \text{ m} \end{aligned}$$

Using Equation 9.24 and Table 9.3, we can write

$$\begin{aligned} \Delta T_f &= K_f m \\ &= (1.86^\circ C \text{ } m^{-1})(4.19 \text{ m}) \\ &= 7.79^\circ C \end{aligned}$$

Because pure water freezes at $0^\circ C$, the solution will freeze at $-7.79^\circ C$. We can calculate boiling-point elevation in the same way:

$$\begin{aligned} \Delta T_b &= K_b m \\ &= (0.52^\circ C \text{ } m^{-1})(4.19 \text{ m}) \\ &= 2.2^\circ C \end{aligned}$$

Because the solution will boil at $100^\circ C + 2.2^\circ C = 102.2^\circ C$, it makes sense to leave the antifreeze in your car radiator in the summer to prevent the solution from boiling.

Practice Exercise Calculate the boiling point and freezing point of a solution containing 478 g of ethylene glycol in 3202 g of water.

Osmotic Pressure

Many chemical and biological processes depend on **osmosis**, *the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one*. Figure 9.19 illustrates this phenomenon. The left compartment of the apparatus contains pure solvent, whereas the right compartment contains a solution of the solvent and some solute. The two compartments are separated by a **semipermeable membrane**, which *allows the passage of solvent molecules but blocks the passage of solute molecules*. At the start, the water levels in the two tubes are equal [see Figure 9.19(a)]. After some time, the level in the right tube begins to rise and continues to increase until equilibrium is reached (i.e., until no further change can be observed). The **osmotic pressure** (Π) of a solution is *the pressure required to stop osmosis*. As shown in Figure 9.19(b), this pressure can be measured directly from the difference in the final fluid levels.

Like freezing-point depression and boiling-point elevation, osmotic pressure can be understood in terms of the free energy of mixing.

If pure solvent is placed on both sides of the semipermeable membrane depicted in Figure 9.19(a), the pressures and molar Gibbs free energies of the liquid in both sides of the container will be equal at equilibrium because the solvent is free to move across the membrane. If we add solute to the solvent on the right-hand side of the membrane, the Gibbs free energy of this solution will be lowered relative to the pure solvent on the left, and the system will no longer be in equilibrium. To restore equilibrium, solvent will move across the membrane from the pure solvent into the solution (i.e., from the left-hand side to the right-hand side). This transfer of matter lowers the Gibbs free energy of the pure solvent, while raising the Gibbs free energy of the solvent in the solution. The transfer stops when the molar Gibbs free energy of the solvent is the same on both sides of the membrane. Because the volume of the solution (right-hand side) is fixed, addition of matter (solvent) at constant T causes a rise in pressure. Similarly, removal of matter from the pure solvent (left-hand side) causes a decrease in pressure, resulting in a pressure imbalance across the membrane at equilibrium.

The osmotic pressure of a solution is given by

$$\Pi = cRT \quad (9.26)$$

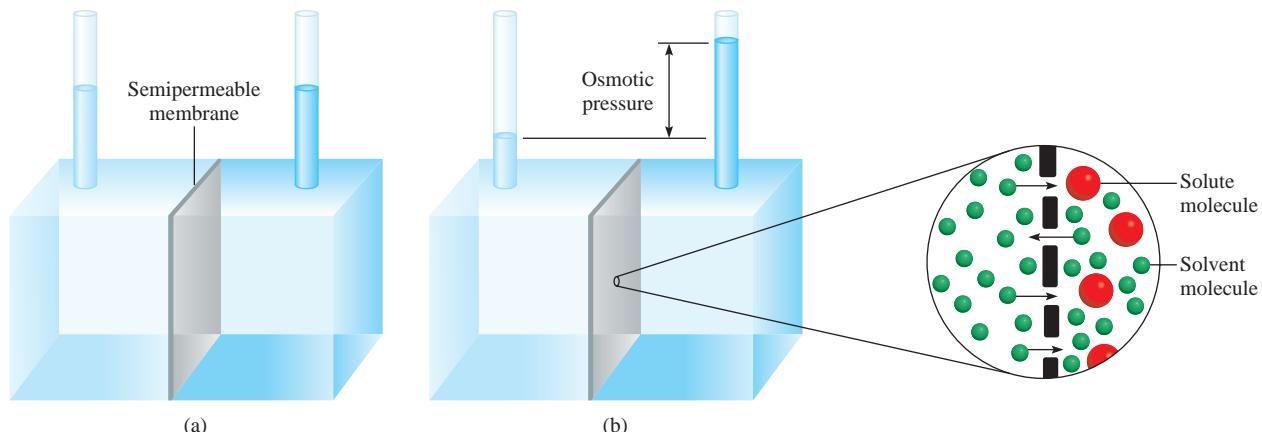


Figure 9.19 Osmotic pressure. (a) The levels of the pure solvent (left) and of the solution (right) are equal at the start. (b) During osmosis, the level of the solution on the solution side rises as a result of the net flow of solvent from left to right. The osmotic pressure is equal to the hydrostatic pressure exerted by the column of fluid in the right tube at equilibrium. The same effect occurs when the pure solvent is replaced by a more dilute solution than that on the right.

where c is the concentration of the solution, R is the gas constant ($0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature. The osmotic pressure (Π), is expressed in bar. Because osmotic pressure measurements are carried out at constant temperature, the concentration (c) is expressed in units of molarity rather than molality. Because the molarity of the solution is given by the number of solute molecules (n_{solute}) divided by the volume (V) of solution ($c = n_{\text{solute}}/V$), Equation 9.26 can also be written as

$$\Pi V = n_{\text{solute}} R T \quad (9.27)$$

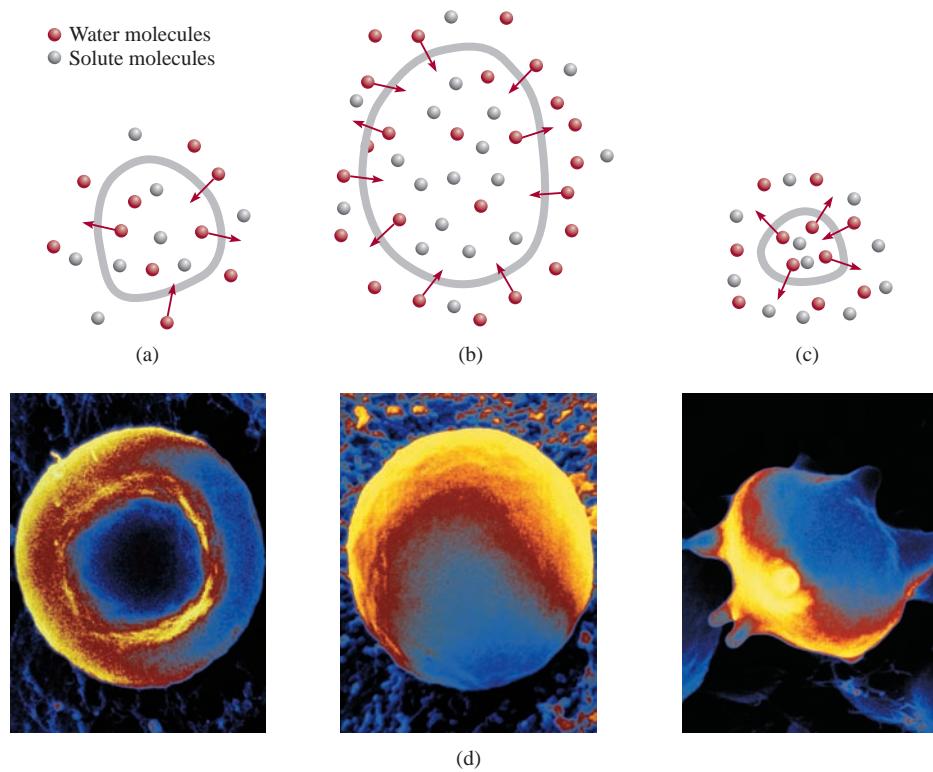
which is often easier to remember than Equation 9.26 because this form is similar to the ideal gas law.

If two solutions have the same concentration and, hence, the same osmotic pressure, they are said to be *isotonic*. If two solutions have different osmotic pressures, the more concentrated solution is said to be *hypertonic* and the more dilute solution is said to be *hypotonic* (Figure 9.20).

Although osmosis is a common and well-studied phenomenon, relatively little is known about how the semipermeable membrane stops some molecules yet allows others to pass. In some cases, it is simply a matter of size. A semipermeable membrane may have pores small enough to let only the solvent molecules through. In other cases, a different mechanism may be responsible for the membrane's selectivity, such as the solvent's greater "solubility" in the membrane.

The osmotic pressure phenomenon manifests itself in many interesting applications. To study the contents of red blood cells, which are protected from the external environment by a semipermeable membrane, biochemists use a technique called *hemolysis*. The red blood cells are placed in a hypotonic solution. Because the hypotonic solution is less concentrated than the interior of the cell, water moves into the cells,

Figure 9.20 A cell in (a) an isotonic solution, (b) a hypotonic solution, and (c) a hypertonic solution. The cell remains unchanged in (a), swells in (b) and shrinks in (c). (d) From left to right: a red blood cell in an isotonic solution, a hypotonic solution, and a hypertonic solution.



as shown in the middle photo of Figure 9.20(d). The cells swell and eventually burst, releasing hemoglobin and other molecules, which are collected and studied. Home preserving of jam and jelly provides another example of the use of osmotic pressure. A large quantity of sugar is actually essential to the preservation process because the sugar helps to kill bacteria that may cause botulism. When a bacterial cell is in a hypertonic (high-concentration) sugar solution, as shown in Figure 9.20(c), the intracellular water tends to move out of the bacterial cell by osmosis to the more concentrated solution. This process, known as *crenation*, causes the cell to shrink and, eventually, to cease functioning. The natural acidity of fruits also inhibits bacteria growth.

Osmotic pressure is the major mechanism for transporting water upward in plants. Because leaves constantly lose water to the air, in a process called *transpiration*, the solute concentrations in leaf fluids increase. Water is pulled up through the trunk, branches, and stems of trees by osmotic pressure. Up to 10 to 15 bar pressure is necessary to transport water to the leaves at the tops of California's redwoods, which reach about 120 m in height.

Example 9.9 shows how an osmotic pressure measurement can be used to determine the concentration of a solution.

Example 9.9

The average osmotic pressure of seawater, measured in the kind of apparatus shown in Figure 9.19, is about 30.0 bar at 25°C. Calculate the molar concentration of an aqueous solution of sucrose ($C_{12}H_{22}O_{11}$) that is isotonic with seawater.

Strategy The sucrose solution is isotonic with seawater, so it has the same concentration and the same osmotic pressure as the seawater.

Solution The aqueous sucrose solution has an osmotic pressure of 30.0 bar because it is isotonic with seawater that has an osmotic pressure of 30.0 bar. Using Equation 9.26,

$$\begin{aligned}\Pi &= cRT \\ c &= \frac{\Pi}{RT} = \frac{30.0 \text{ bar}}{(0.08314 \text{ L bar K}^{-1})(298 \text{ K})} \\ &= 1.23 \text{ mol L}^{-1} \\ &= 1.23 M\end{aligned}$$

Practice Exercise What is the osmotic pressure (in bar) of a 0.884 M urea solution at 16°C?



California redwoods

Using Colligative Properties to Determine Molar Mass

The colligative properties of nonelectrolyte solutions provide a means of determining the molar mass of a solute. Theoretically, any of the four colligative properties is suitable for this purpose. In practice, however, only freezing-point depression and osmotic pressure are used because they exhibit the most pronounced colligative effects, that is, they exhibit the largest temperature changes for a given molarity and generate measurable effects for even very small concentrations. The procedure is as follows. From the experimentally determined freezing-point depression or osmotic pressure, we can calculate the molality or molarity of the solution. Knowing the mass of the solute, we can readily determine its molar mass, as shown in Examples 9.10 and 9.11.

Example 9.10

A 7.85-g sample of a compound with the empirical formula C₅H₄ is dissolved in 301 g of benzene. The freezing point of the solution is 1.05°C below that of pure benzene. What are the molar mass and molecular formula of this compound?

Strategy Solving this problem requires three steps. First, we calculate the molality of the solution from the freezing-point depression. Next, from the molality we determine the number of moles in 7.85 g of the compound and hence its molar mass. Finally, comparing the experimental molar mass with the empirical molar mass enables us to write the molecular formula.

Solution The sequence of conversions for calculating the molar mass of the compound is as follows:



To calculate the molality of the solution, use Equation 9.24 and the appropriate value of K_f from Table 9.3:

$$\text{molality} = \frac{\Delta T_f}{K_f} = \frac{1.05^\circ\text{C}}{5.12^\circ\text{C } m^{-1}} = 0.205 \text{ } m$$

Because there is 0.205 mole of the solute in 1 kg of solvent, the number of moles of solute in 301 g, or 0.301 kg, of solvent is

$$0.301 \text{ kg} \times \frac{0.205 \text{ mol}}{1 \text{ kg}} = 0.0617 \text{ mol}$$

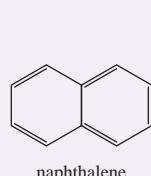
Thus, the molar mass of the solute is

$$\text{molar mass} = \frac{\text{grams of compound}}{\text{moles of compound}} = \frac{7.85 \text{ g}}{0.0617 \text{ mol}} = 127 \text{ g mol}^{-1}$$

Now we can determine the ratio of the molar mass to the empirical molar mass:

$$\frac{\text{molar mass}}{\text{empirical molar mass}} = \frac{127 \text{ g mol}^{-1}}{64 \text{ g mol}^{-1}} \approx 2$$

Thus, the molecular formula is (C₅H₄)₂ or C₁₀H₈. This does not give us, however, enough information to identify the compound as there are at least two compounds that have this molecular formula, namely, naphthalene and azulene:



Practice Exercise A solution of 0.85 g of an organic compound in 100.0 g of benzene has a freezing point of 5.16°C. What are the molality of the solution and the molar mass of the solute?

Example 9.11

A solution is prepared by dissolving 35.0 g of hemoglobin (Hb) in enough water to make up 1 L in volume. If the osmotic pressure of the solution is found to be 10.0 mmHg at 25°C, calculate the molar mass of hemoglobin.

Strategy The steps needed to calculate the molar mass of Hb are similar to those outlined in Example 9.10, except we use osmotic pressure instead of freezing-point depression. First, we must calculate the molarity of the solution from the osmotic pressure of the solution. Then, from the molarity, we can determine the number of moles in 35.0 g of Hb and hence its molar mass. Because the pressure is given in mmHg, it is more convenient to use R in terms of L atm instead of L bar because the conversion factor from mm Hg to atm is simpler.

Solution The sequence of conversions is as follows:



First, calculate the molarity using Equation 9.26:

$$\begin{aligned} \Pi &= cRT \\ c &= \frac{\Pi}{RT} \\ &= \frac{10.0 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 5.38 \times 10^{-4} \text{ M} \end{aligned}$$

The volume of the solution is 1 L, so it must contain 5.38×10^{-4} mol of Hb. We use this quantity to calculate the molar mass:

$$\text{molar mass of Hb} = \frac{\text{grams of Hb}}{\text{moles of Hb}} = \frac{35.0 \text{ g}}{5.38 \times 10^{-4} \text{ mol}} = 6.51 \times 10^4 \text{ g mol}^{-1}$$

Practice Exercise A 202-mL benzene solution containing 2.47 g of an organic polymer has an osmotic pressure of 8.63 mmHg at 21°C. Calculate the molar mass of the polymer.

A pressure of 10.0 mmHg, like the one in Example 9.11, can be measured easily and accurately. As a result, osmotic pressure measurements are very useful for determining the molar masses of large molecules, such as proteins. To see how much more practical the osmotic pressure technique is than freezing-point depression would be, let us estimate the change in freezing point of the hemoglobin solution from Example 9.11. If an aqueous solution is quite dilute, we can assume that molarity is roughly equal to molality. (Molarity would be equal to molality if the density of the aqueous solution were 1 g mL⁻¹.) Hence, from Equation 9.24 we can write

$$\Delta T_f = (1.86^\circ\text{C } m^{-1})(5.38 \times 10^{-4} \text{ m}) = 1.00 \times 10^{-3}^\circ\text{C}$$

The freezing-point depression of one-thousandth of a degree is too small of a temperature change to measure accurately. For this reason, the freezing-point depression technique is more suitable for determining the molar mass of smaller and more soluble

molecules, those having molar masses of 500 g or less, because the freezing-point depressions of their solutions are much greater.

Colligative Properties of Electrolyte Solutions

The study of the colligative properties of *electrolytes* (*substances that dissociate into ions in solution*) requires a slightly different approach than the one used for the colligative properties of nonelectrolytes. One unit of an electrolyte compound yields two or more particles when it dissolves. Because it is the number of solute particles that determines the colligative properties of a solution, it is important to know which compounds dissociate and to what extent. For example, each unit of NaCl dissociates into two ions, Na^+ and Cl^- , so the colligative properties of a 0.1 *m* NaCl solution should be twice as great as those of a 0.1 *m* solution containing a nonelectrolyte, such as sucrose. Similarly, a 0.1 *m* CaCl_2 solution depresses the freezing point by three times as much as a 0.1 *m* sucrose solution because each CaCl_2 produces three ions. To account for this effect, there is a quantity called the *van't Hoff⁵ factor* (*i*) given by the following:

$$i = \frac{\text{actual number of particles in solution after dissociation}}{\text{number of formula units initially dissolved in solution}} \quad (9.28)$$

Thus, *i* should be 1 for all nonelectrolytes. For strong electrolytes such as NaCl and KNO_3 , *i* should be 2, and for strong electrolytes such as Na_2SO_4 and CaCl_2 , *i* should be 3. Consequently, the equations for colligative properties must be modified as follows:

$$\Delta T_b = iK_b m_B \quad (9.29)$$

$$\Delta T_f = iK_f m_B \quad (9.30)$$

$$\Pi = i c R T \quad (9.31)$$

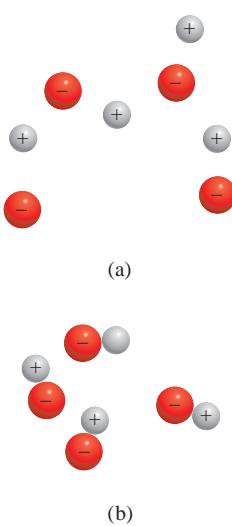


Figure 9.21 (a) Free ions and (b) ion pairs in solution. An ion pair bears no net charge, so it cannot conduct electricity in solution.

In reality, the colligative properties of electrolyte solutions are usually less than anticipated because at higher concentrations ($> \sim 0.01 \text{ M}$), electrostatic forces come into play and bring about the formation of ion pairs. An *ion pair* is made up of *one or more cations and one or more anions held together by electrostatic forces*. The presence of an ion pair reduces the effective number of particles in solution, causing a reduction in the colligative properties (Figure 9.21). Electrolytes containing multi-charged ions such as Mg^{2+} , Al^{3+} , and Fe^{2+} have a greater tendency to form ion pairs than electrolytes such as NaCl and KNO_3 , which are made up of singly charged ions. Noninteger values of the van't Hoff factor are necessary to compensate for the deviation from ideal-solution behavior exhibited by electrolyte solutions because of ion-pair formation.

Table 9.4 lists the experimentally measured values of *i* and those calculated assuming complete dissociation. The agreement is close but not perfect, indicating that the extent of ion-pair formation in these solutions at 0.0500 *M* concentration is appreciable.

5. Jacobus Hendricus van't Hoff (1852–1911). Dutch chemist. One of the most prominent chemists of his time, van't Hoff did significant work in thermodynamics, molecular structure and optical activity, and solution chemistry. In 1901, he received the first Nobel Prize in Chemistry.

Table 9.4 The van't Hoff Factor of 0.0500 M Electrolyte Solutions at 25°C

| Electrolyte | <i>i</i> (Measured) | <i>i</i> (Calculated) |
|-------------------|---------------------|-----------------------|
| Sucrose* | 1.0 | 1.0 |
| HCl | 1.9 | 2.0 |
| NaCl | 1.9 | 2.0 |
| MgSO ₄ | 1.3 | 2.0 |
| MgCl ₂ | 2.7 | 3.0 |
| FeCl ₃ | 3.4 | 4.0 |

*Sucrose is a nonelectrolyte. It is listed here for comparison only.

Example 9.12 shows how the van't Hoff factor can be determined from colligative properties measurements.

Example 9.12

The osmotic pressure of a 0.010 M potassium iodide (KI) solution at 25°C is 0.471 bar. Calculate the van't Hoff factor for KI at this concentration.

Strategy KI is a strong electrolyte, so it should dissociate completely in solution. If so, its osmotic pressure would be

$$2(0.010 \text{ M})(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(298 \text{ K}) = 0.496 \text{ bar}$$

The measured osmotic pressure, however, is only 0.471 bar. This value is less than predicted, indicating that ion pairs are forming, thus reducing the number of solute particles (K⁺ and I⁻ ions) in solution.

Solution From Equation 9.31, we have

$$i = \frac{\Pi}{MRT} = \frac{0.471 \text{ bar}}{(0.010 \text{ M})(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 1.90$$

Practice Exercise The freezing-point depression of a 0.100 m MgSO₄ solution is 0.225°C. Calculate the van't Hoff factor for MgSO₄ at this concentration.

Summary of Facts and Concepts

Section 9.1

- The shapes of the phase boundaries in a phase diagram can be determined from thermodynamics using the Clapeyron equation. If one of the phases is a vapor, then the Clausius-Clapeyron approximation can be used.

Section 9.2

- The ease of dissolving a solute in a solvent is governed by intermolecular forces. The enthalpy and entropy of

mixing are the forces driving the solution process. These effects can be roughly summarized by the concept of *like dissolves like*.

- Increasing temperature usually increases the solubility of solid and liquid substances and usually decreases the solubility of gases in water.
- According to Henry's law, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas over the solution.

Section 9.3

- Raoult's law states that the partial pressure of a substance A over a solution is equal to the mole fraction (x_A) of A times the vapor pressure (P_A^*) of pure A. An ideal solution obeys Raoult's law over the entire range of concentration. In practice, very few solutions exhibit ideal behavior.
- Raoult's law can be used to determine the vapor pressure and composition of the vapor above a solution of two volatile liquids.
- Deviations from ideal solution behavior can be understood in terms of the intermolecular forces.

Section 9.4

- Vapor-pressure lowering, boiling-point elevation, freezing-point depression, and osmotic pressure are colligative properties of solutions, that is, they depend only on the number of solute particles that are present and not on their nature.
- In electrolyte solutions, the interaction between ions leads to the formation of ion pairs. The van't Hoff factor provides a measure of the extent of dissociation of electrolytes in solution.

Key Words

azeotrope, p. 490
 boiling-point elevation, p. 493
 Clapeyron equation, p. 468
 Clausius-Clapeyron equation, p. 471
 colligative properties, p. 491
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Problems

The Phase Boundaries in Pure Substances Can Be Predicted Using Thermodynamics

- 9.1 A length of wire is placed on top of a block of ice. The ends of the wire extend over the edges of the ice, and a heavy weight is attached to each end. It is found that the ice under the wire gradually melts, and that the wire then slowly moves through the ice block. At the same time, the water above the wire refreezes. Give an explanation for this observation.
- 9.2 Vapor pressure measurements at several different temperatures are shown here for mercury. (a) Determine graphically the molar heat of vaporization for mercury.

| T (°C) | 200 | 250 | 300 | 320 | 340 |
|------------|------|------|-------|-------|-------|
| P (mmHg) | 17.3 | 74.4 | 246.8 | 376.3 | 557.9 |

(b) Use the results from this experiment to predict the normal boiling temperature of mercury. Does this temperature agree with the experimental value given in Table 7.7? If not, give some possible origins for this discrepancy.

- 9.3 The vapor pressure of benzene (C_6H_6) is 40.1 mmHg at 7.6°C. What is its vapor pressure at 60.6°C? The molar heat of vaporization of benzene is 31.0 kJ mol⁻¹.
- 9.4 The vapor pressure of liquid X is lower than that of liquid Y at 20°C, but higher at 60°C. What can you deduce about the relative magnitude of the molar heats of vaporization of X and Y?
- 9.5 Estimate the molar heat of vaporization of a liquid whose vapor pressure doubles when the temperature is raised from 85°C to 95°C.
- 9.6 In Example 9.1, we used the Clapeyron equation to predict that the melting point of water decreases by 1°C for every 138 bar increase in pressure. Using this, one could predict that at a pressure of about 3.8×10^4 bar ($= 273^\circ\text{C} \times 138 \text{ bar} \text{ }^\circ\text{C}^{-1}$) the melting point of water would be -273.15°C or 0 K (absolute zero). Is this prediction reasonable? If not, explain where it went wrong.

The Solubility of a Substance Is Determined by Temperature, Pressure, and Intermolecular Forces

- 9.7 Why is naphthalene ($C_{10}H_8$) more soluble in benzene than CsF?
- 9.8 Why is ethanol (C_2H_5OH) insoluble in cyclohexane (C_6H_{12})?
- 9.9 Arrange the following compounds in order of increasing solubility in water: O_2 , LiCl, Br_2 , and methanol (CH_3OH).
- 9.10 Explain the variations in solubility in water of the alcohols listed here:

| Compound | Solubility in Water (g/100 g) at 20°C |
|--------------------------|--|
| CH_3OH | ∞ |
| CH_3CH_2OH | ∞ |
| $CH_3CH_2CH_2OH$ | ∞ |
| $CH_3CH_2CH_2CH_2OH$ | 9 |
| $CH_3CH_2CH_2CH_2CH_2OH$ | 2.7 |

- 9.11 A 3.20-g sample of a salt dissolves in 9.10 g of water to give a saturated solution at 25°C. What is the solubility (in g salt/100 g of H_2O) of the salt?
- 9.12 The solubility of KNO_3 is 155 g/100 g of water at 75°C but only 38.0 g/100 g of water at 25°C. What mass (in grams) of KNO_3 will crystallize out of solution if exactly 100 g of its saturated solution at 75°C is cooled to 25°C?
- 9.13 A 50-g sample of impure $KClO_3$ (solubility = 7.1 g per 100 g H_2O at 20°C) is contaminated with 10 percent KCl (solubility = 25.5 g per 100 g of H_2O at 20°C). Calculate the minimum quantity of water at 20°C that is needed to dissolve all the KCl from the sample. How much $KClO_3$ will be left after this treatment? (Assume that the solubilities are unaffected by the presence of the other compound.)
- 9.14 A beaker of water is initially saturated with dissolved air. Explain what happens when He gas at 1 bar is bubbled through the solution for a long time.
- 9.15 A miner working 260 m below sea level opened a carbonated soft drink during a lunch break. To his surprise, the soft drink tasted rather “flat.” Shortly afterward, the miner took an elevator to the surface. During the trip up, he could not stop belching. Why?
- 9.16 The solubility of CO_2 in water at 25°C and 1 bar is 0.034 mol L^{-1} . What is its solubility under atmospheric conditions? (The partial pressure of CO_2 in air is 0.0003 atm.) Assume that CO_2 obeys Henry’s law.
- 9.17 The solubility of N_2 in blood at 37°C and at a partial pressure of 0.80 bar is $5.6 \times 10^{-4}\text{ mol/L}$. A deep-sea diver breathes compressed air with the partial pressure of N_2 equal to 4.0 bar. Assume that the total

volume of blood in the diver’s body is 5.0 L. Calculate the amount of N_2 gas released (in liters at 37°C and 1 bar) when the diver returns to the surface of the water where the partial pressure of N_2 is 0.80 bar.

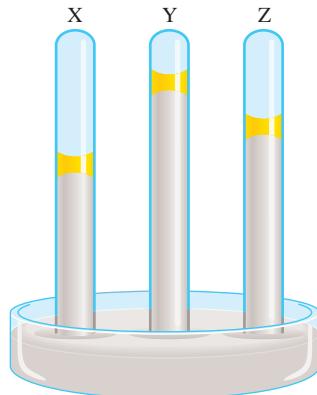
The Liquid-Vapor Phase Equilibrium of a Solution Can Be Understood in Terms of the Entropy of Mixing and Intermolecular Forces

- 9.18 The vapor pressures of ethanol (C_2H_5OH) and 1-propanol (C_3H_7OH) at 35°C are 100 and 37.6 mmHg, respectively. Assume ideal behavior and calculate the partial pressures of ethanol and 1-propanol at 35°C over a solution of ethanol in 1-propanol, in which the mole fraction of ethanol is 0.300.
- 9.19 At 20°C, the vapor pressure of ethanol (C_2H_5OH) is 44 mmHg and the vapor pressure of methanol (CH_3OH) is 94 mmHg. A mixture of 30.0 g of methanol and 45.0 g of ethanol is prepared (and can be assumed to behave as an ideal solution). (a) Calculate the vapor pressure of methanol and ethanol above this solution at 20°C. (b) Calculate the mole fraction of methanol and ethanol in the vapor above this solution at 20°C. (c) Suggest a method for separating the two components of the solution.
- 9.20 A mixture of liquids A and B exhibits ideal behavior. At 84°C, the total vapor pressure of a solution containing 1.2 moles of A and 2.3 moles of B is 331 mm Hg. Upon the addition of another mole of B to the solution, the vapor pressure increases to 347 mmHg. Calculate the vapor pressures of pure A and pure B at 84°C.
- 9.21 Explain in terms of molecular interactions why the temperature-composition phase diagram for chloroform and acetone possesses a high-boiling azeotrope.
- 9.22 If you try to purify ethanol from an ethanol-water mixture by fractional distillation, the maximum purity obtainable is 95 percent. Explain.
- ### Colligative Properties Are Properties of Solution Phase Equilibria That Depend Only upon the Number of Solute Molecules, Not Their Type
- 9.23 A solution is prepared by dissolving 396 g of sucrose ($C_{12}H_{22}O_{11}$) in 624 g of water. What is the vapor pressure of this solution at 30°C? (The vapor pressure of water is 31.8 mmHg at 30°C.)
- 9.24 How many grams of sucrose ($C_{12}H_{22}O_{11}$) must be added to 552 g of water to give a solution with a vapor pressure 2.0 mmHg less than that of pure water at 20°C? (The vapor pressure of water at 20°C is 17.5 mmHg.)
- 9.25 The vapor pressure of benzene is 100.0 mmHg at 26.1°C. Calculate the vapor pressure of a solution containing 24.6 g of camphor ($C_{10}H_{16}O$) dissolved in 98.5 g of benzene. (Camphor is a low-volatility solid.)

- 9.26 How many grams of urea $[(\text{NH}_2)_2\text{CO}]$ must be added to 450 g of water to give a solution with a vapor pressure 2.50 mmHg less than that of pure water at 30°C? (The vapor pressure of water at 30°C is 31.8 mmHg.)
- 9.27 What are the boiling point and freezing point of a 2.47 *m* solution of naphthalene in benzene? (The boiling point and freezing point of benzene are 80.1°C and 5.5°C, respectively.)
- 9.28 An aqueous solution contains the amino acid glycine ($\text{NH}_2\text{CH}_2\text{COOH}$). Assuming that the acid does not ionize in water, calculate the molality of the solution if it freezes at -1.1°C .
- 9.29 Pheromones are compounds secreted by the females of many insect species to attract males. One of these compounds contains 80.78 percent C, 13.56 percent H, and 5.66 percent O. A solution of 1.00 g of this pheromone in 8.50 g of benzene freezes at 3.37°C. What are the molecular formula and molar mass of the compound? (The normal freezing point of pure benzene is 5.50°C.)
- 9.30 The elemental analysis of an organic solid extracted from gum arabic (a gummy substance used in adhesives, inks, and pharmaceuticals) showed that it contained 40.0 percent C, 6.7 percent H, and 53.3 percent O. A solution of 0.650 g of the solid in 27.8 g of the solvent diphenyl gave a freezing-point depression of 1.56°C . Calculate the molar mass and molecular formula of the solid. (K_f for diphenyl is $8.00^\circ\text{C}\text{ }m^{-1}$.)
- 9.31 How many liters of the antifreeze ethylene glycol [$\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$] would you add to a car radiator containing 6.50 L of water if the coldest winter temperature in your area is -20°C ? Calculate the boiling point of this water/ethylene glycol mixture. (The density of ethylene glycol is 1.11 g mL^{-1} .)
- 9.32 A solution is prepared by condensing 4.00 L of a gas, measured at 27°C and 748 mmHg pressure, into 58.0 g of benzene. Calculate the freezing point of this solution.
- 9.33 The molar mass of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) determined by measuring the freezing-point depression in benzene is twice what we would expect for the molecular formula $\text{C}_7\text{H}_6\text{O}_2$. Explain this apparent anomaly.
- 9.34 A solution of 2.50 g of a compound having the empirical formula $\text{C}_6\text{H}_5\text{P}$ in 25.0 g of benzene is observed to freeze at 4.3°C . Calculate the molar mass of the solute and determine its molecular formula.
- 9.35 What is the osmotic pressure (in bar) of a 1.36 *M* aqueous solution of urea $[(\text{NH}_2)_2\text{CO}]$ at 22.0°C ?
- 9.36 A solution containing 0.8330 g of a polymer of unknown structure in 170.0 mL of an organic solvent was found to have an osmotic pressure of 5.20 mmHg at 25°C . Determine the molar mass of the polymer.
- 9.37 A quantity of 7.480 g of an organic compound is dissolved in water to make 300.0 mL of solution. The solution has an osmotic pressure of 1.45 bar at 27°C . The analysis of this compound shows that it contains 41.8 percent C, 4.7 percent H, 37.3 percent O, and 16.3 percent N. Determine the molecular formula of the compound.
- 9.38 A solution of 6.85 g of a carbohydrate in 100.0 g of water has a density of 1.024 g mL^{-1} and an osmotic pressure of 4.670 bar at 20.0°C . Calculate the molar mass of the carbohydrate.
- 9.39 Which aqueous solution, 0.35 *m* CaCl_2 or 0.90 *m* urea, has (a) the higher boiling point, (b) the higher freezing point, and (c) the lower vapor pressure? Explain. Assume complete dissociation.
- 9.40 Aqueous solutions of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) and of nitric acid (HNO_3) both freeze at 1.5°C . What other properties do these solutions have in common?
- 9.41 Arrange the following solutions in order of decreasing freezing point: 0.10 *m* Na_3PO_4 , 0.35 *m* NaCl , 0.20 *m* MgCl_2 , 0.15 *m* $\text{C}_6\text{H}_{12}\text{O}_6$, and 0.15 *m* CH_3COOH .
- 9.42 Arrange the following aqueous solutions in order of decreasing freezing point: 0.50 *m* HCl , 0.50 *m* glucose, and 0.50 *m* acetic acid. Explain your reasoning.
- 9.43 What are the normal freezing points and boiling points of (a) 21.2 g NaCl in 135 mL of water and (b) 15.4 g of urea in 66.7 mL of water?
- 9.44 At 25°C , the vapor pressure of pure water is 23.76 mmHg and that of seawater is 22.98 mmHg. Assuming that seawater contains only NaCl , estimate its molal concentration.
- 9.45 Both NaCl and CaCl_2 are used to melt ice on roads and sidewalks in winter. What advantages do these substances have over sucrose or urea in lowering the freezing point of water?
- 9.46 A 0.86 percent by mass solution of NaCl is called “physiological saline” because its osmotic pressure is equal to that of the solution in blood cells. Calculate the osmotic pressure of this solution at normal body temperature (37°C). The density of the saline solution is 1.005 g mL^{-1} .
- 9.47 The osmotic pressure of 0.010 *M* solutions of CaCl_2 and urea at 25°C are 0.613 and 0.247 bar, respectively. Calculate the van't Hoff factor for the CaCl_2 solution.
- 9.48 Calculate the osmotic pressure of a 0.0500 *M* MgSO_4 solution at 25°C . (Hint: See Table 9.4.)

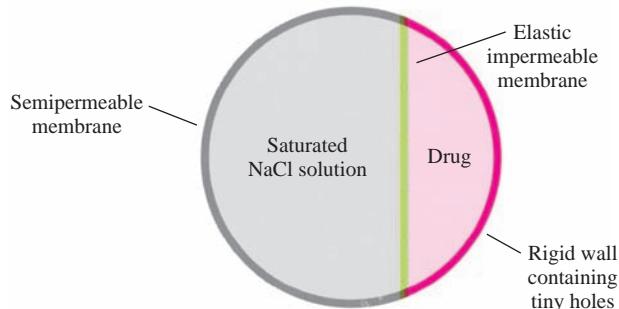
Additional Problems

- 9.49 A beaker of water is placed in a closed container. Predict the effect on the vapor pressure of water when (a) the temperature is lowered, (b) the volume of the container is doubled, and (c) more water is added to the beaker.
- 9.50 The south pole of Mars is covered with dry ice, which partially sublimes during the summer. The CO_2 vapor recondenses in the winter when the temperature drops to 150 K. Given that the heat of sublimation of CO_2 is 25.9 kJ mol⁻¹, calculate the atmospheric pressure on the surface of Mars. The normal sublimation temperature of CO_2 is -78°C.
- 9.51 A pressure cooker is a sealed container that allows steam to escape when it exceeds a predetermined pressure. How does this device reduce the time needed for cooking?
- 9.52 Lysozyme is an enzyme that cleaves bacterial cell walls. A sample of lysozyme extracted from egg white has a molar mass of 13,930 g. A quantity of 0.100 g of this enzyme is dissolved in 150 g of water at 25°C. Calculate the vapor-pressure lowering, the depression in freezing point, the elevation in boiling point, and the osmotic pressure of this solution. (The vapor pressure of water at 25°C is 23.76 mmHg.)
- 9.53 Solutions A and B have osmotic pressures of 2.4 and 4.6 bar, respectively, at a certain temperature. What is the osmotic pressure of a solution prepared by mixing equal volumes of A and B at the same temperature?
- 9.54 A cucumber placed in concentrated brine (saltwater) shrivels into a pickle. Explain.
- 9.55 Two liquids A and B have vapor pressures of 76 and 132 mmHg, respectively, at 25°C. What is the total vapor pressure of the ideal solution made up of (a) 1.00 mole of A and 1.00 mole of B, and (b) 2.00 moles of A and 5.00 moles of B?
- 9.56 Calculate the van't Hoff factor of Na_3PO_4 in a 0.40 *m* solution whose freezing point is 2.6°C.
- 9.57 A 262-mL sample of a sugar solution containing 1.22 g of the sugar has an osmotic pressure of 30.3 mmHg at 35°C. What is the molar mass of the sugar?
- 9.58 Consider the three mercury manometers shown in the diagram. One of them has 1 mL of water on top of the mercury, another has 1 mL of a 1 *m* urea solution on top of the mercury, and the third one has 1 mL of a 1 *M* NaCl solution placed on top of the mercury. Which of these solutions is in the tube labeled X, which is in Y, and which is in Z?



- 9.59 A forensic chemist is given a white powder for analysis. She dissolves 0.50 g of the substance in 8.0 g of benzene. The solution freezes at 3.9°C. Can the chemist conclude that the compound is cocaine ($\text{C}_{17}\text{H}_{21}\text{NO}_4$)? What assumptions are made in the analysis?

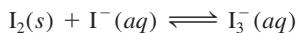
- 9.60 "Time-release" drugs have the advantage of releasing the drug to the body at a constant rate so that the drug concentration at any time is not too high as to have harmful side effects or too low as to be ineffective. A schematic diagram of a pill that works on this basis is shown here. Explain how it works.



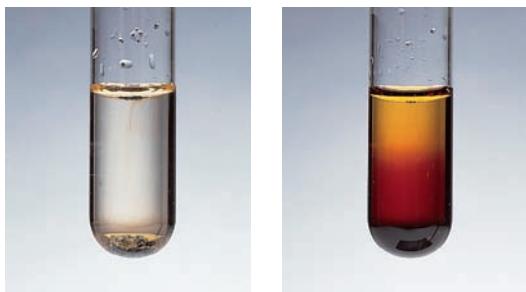
- 9.61 A solution of 1.00 g of anhydrous aluminum chloride (AlCl_3) in 50.0 g of water freezes at -1.11°C. Does the molar mass determined from this freezing point agree with that calculated from the formula? Why?
- 9.62 Explain why reverse osmosis is (theoretically) more desirable as a desalination method than distillation or freezing. What minimum pressure must be applied to seawater at 25°C in order for reverse osmosis to occur? (Treat seawater as a 0.70 *M* NaCl solution.)
- 9.63 A protein has been isolated as a salt with the formula Na_{20}P (this notation means that there are 20 Na^+ ions associated with a negatively charged protein P^{20-}). The osmotic pressure of a 10.0-mL solution containing 0.225 g of the protein is 0.260 bar at

25.0°C. (a) Calculate the molar mass of the protein from these data. (b) Calculate the actual molar mass of the protein.

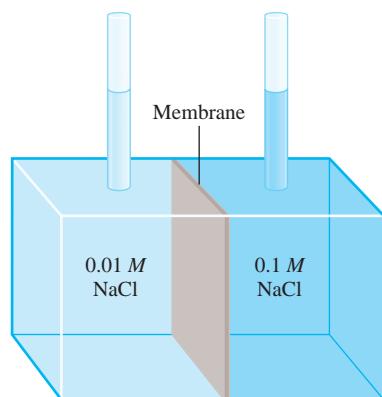
- 9.64 A nonvolatile organic compound Z was used to make up two solutions. Solution A contains 5.00 g of Z dissolved in 100 g of water, and solution B contains 2.31 g of Z dissolved in 100 g of benzene. Solution A has a vapor pressure of 754.5 mmHg at the normal boiling point of water, and solution B has the same vapor pressure at the normal boiling point of benzene. Calculate the molar mass of Z in solutions A and B and account for the difference.
- 9.65 State which of the alcohols listed in Problem 9.10 you would expect to be the best solvent for each of the following substances, and explain why: (a) I₂, (b) KBr, and (c) CH₃CH₂CH₂CH₂CH₃.
- 9.66 Before a carbonated beverage bottle is sealed, it is pressurized with a mixture of air and carbon dioxide. (a) Explain the effervescence that occurs when the cap of the bottle is removed. (b) What causes the fog to form near the mouth of the bottle right after the cap is removed?
- 9.67 Iodine (I₂) is only sparingly soluble in water (see left photo). Yet upon the addition of iodide ions (for example, from KI), iodine is converted to the triiodide ion, which readily dissolves (right photo):



Describe the change in solubility of I₂ in terms of the change in intermolecular forces.



- 9.68 Two beakers, one containing a 50-mL aqueous 1.0 M glucose solution and the other a 50-mL aqueous 2.0 M glucose solution, are placed under a tightly sealed bell jar at room temperature. What are the volumes in these two beakers at equilibrium?
- 9.69 In the apparatus shown here, what will happen if the membrane is (a) permeable to both water and the Na⁺ and Cl⁻ ions, (b) permeable to water and Na⁺ ions but not to Cl⁻ ions, (c) permeable to water but not to Na⁺ and Cl⁻ ions?



- 9.70 Explain why it is essential that fluids used in intravenous injections have approximately the same osmotic pressure as blood.
- 9.71 Explain each of the following statements: (a) The boiling point of seawater is higher than that of pure water. (b) Carbon dioxide escapes from the solution when the cap is removed from a carbonated soft drink bottle. (c) Molal and molar concentrations of dilute aqueous solutions are approximately equal. (d) In discussing the colligative properties of a solution (other than osmotic pressure), it is preferable to express the concentration in units of molality rather than in molarity. (e) Methanol (b.p. 65°C) is useful as an antifreeze, but it should be removed from the car radiator during the summer season.
- 9.72 A mixture of NaCl and sucrose (C₁₂H₂₂O₁₁) of combined mass 10.2 g is dissolved in enough water to make up a 250 mL solution. The osmotic pressure of the solution is 7.42 bar at 23°C. Calculate the mass percent of NaCl in the mixture.
- 9.73 A 1.32-g sample of a mixture of cyclohexane (C₆H₁₂) and naphthalene (C₁₀H₈) is dissolved in 18.9 g of benzene (C₆H₆). The freezing point of the solution is 2.2°C. Calculate the mass percent of the mixture. (See Table 9.3 for constants.)
- 9.74 How does each of the following affect the solubility of an ionic compound: (a) lattice energy, (b) solvent (polar versus nonpolar), and (c) enthalpies of hydration of cation and anion?
- 9.75 A solution contains two volatile liquids A and B. Complete the following table, in which the symbol \longleftrightarrow indicates attractive intermolecular forces.

| Attractive Forces | Deviation from Raoult's Law | ΔH_{soln} |
|---|-----------------------------|--------------------------|
| A \longleftrightarrow A, B \longleftrightarrow B > A \longleftrightarrow B | | |
| | Negative | |
| | | Zero |

- 9.76 A mixture of ethanol and 1-propanol behaves ideally at 36°C and is in equilibrium with its vapor. If the mole fraction of ethanol in the solution is 0.62, calculate its mole fraction in the vapor phase at this temperature. (The vapor pressures of pure ethanol and 1-propanol at 36°C are 108 and 40.0 mmHg, respectively.)
- 9.77 For ideal solutions, the volumes are additive. This means that if 5 mL of A and 5 mL of B form an ideal solution, the volume of the solution is 10 mL. Provide a molecular interpretation for this observation. When 500 mL of ethanol (C_2H_5OH) are mixed with 500 mL of water, the final volume is less than 1000 mL. Why?
- 9.78 Ammonia (NH_3) is very soluble in water, but nitrogen trichloride (NCl_3) is not. Explain.
- 9.79 Aluminum sulfate [$Al_2(SO_4)_3$] is sometimes used in municipal water treatment plants to remove undesirable particles. Explain how this process works.
- 9.80 Acetic acid is a weak acid that ionizes in solution as follows:
- $$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$
- If the freezing point of a 0.106 m CH_3COOH solution is 0.203°C, calculate the percent of the acid that has undergone ionization.
- 9.81 Making mayonnaise involves beating oil into small droplets in water, in the presence of egg yolk. What is the purpose of the egg yolk? (Hint: Egg yolk contains lecithins, which are molecules with a polar head and a long nonpolar hydrocarbon tail.)
- 9.82 Acetic acid is a polar molecule and can form hydrogen bonds with water molecules. Therefore, it has a high solubility in water. Yet acetic acid is also soluble in benzene (C_6H_6), a nonpolar solvent that lacks the ability to form hydrogen bonds. A solution of 3.8 g of CH_3COOH in 80 g C_6H_6 has a freezing point of 3.5°C. Calculate the molar mass of the solute and suggest what its structure might be. (Hint: Acetic acid molecules can form hydrogen bonds between themselves.)
- 9.83 Fish in the Antarctic Ocean swim in water at about -2°C. (a) To prevent their blood from freezing, what must be the concentration (in molality) of the blood? Is this a reasonable physiological concentration? (b) In recent years scientists have discovered a special type of protein in these fishes' blood which, although present in quite low concentrations ($\leq 0.001\text{ }m$), has the ability to prevent the blood from freezing. Suggest a mechanism for its action.
- 9.84 As we know, if a soft drink can is shaken and then opened, the drink escapes violently. However, if after shaking the can we tap it several times with a metal spoon, no such "explosion" of the drink occurs. Why?
- 9.85 Why are ice cubes (for example, those you see in the trays in the freezer of a refrigerator) cloudy inside?
- 9.86 Using Henry's law and the ideal gas equation, prove the statement that the volume of a gas that dissolves in a given amount of solvent is *independent* of the pressure of the gas dissolved in the solvent.
- 9.87 At 27°C, the vapor pressure of pure water is 23.76 mmHg and that of an urea solution is 22.98 mmHg. Calculate the molality of the solution.
- 9.88 An example of the positive deviation from Raoult's law is a solution made of acetone (CH_3COCH_3) and carbon disulfide (CS_2). (a) Draw Lewis structures of these molecules. Explain the deviation from ideal behavior in terms of intermolecular forces. (b) A solution composed of 0.60 mole of acetone and 0.40 mole of carbon disulfide has a vapor pressure of 615 mmHg at 35.2°C. What would be the vapor pressure if the solution behaved ideally? The vapor pressure of the pure solvents at the same temperature are: 349 mmHg for acetone and 501 mmHg for carbon disulfide. (c) Predict the sign of ΔH_{soln} .
- 9.89 Liquids A (molar mass 100 g mol^{-1}) and B (molar mass 110 g mol^{-1}) form an ideal solution. At 55°C, A has a vapor pressure of 95 mmHg and B has a vapor pressure of 42 mmHg. A solution is prepared by mixing equal masses of A and B. (a) Calculate the mole fraction of each component in the solution. (b) Calculate the partial pressures of A and B over the solution at 55°C. (c) Suppose that some of the vapor described in part (b) is condensed to a liquid. Calculate the mole fraction of each component in this liquid and the vapor pressure of each component above this liquid at 55°C.
- 9.90 A very long pipe is capped at one end with a semipermeable membrane. How deep (in meters) must the pipe be immersed into the sea for freshwater to begin to pass through the membrane? Assume the water to be at 20°C and treat it as a 0.70 M $NaCl$ solution. The density of seawater is 1.03 g cm^{-3} , and the acceleration due to gravity is 9.81 $m\text{ s}^{-2}$.
- 9.91 Benzene and toluene form an ideal solution. Prove that the maximum entropy of mixing in the liquid is obtained when the mole fraction of each component is 0.5.
- 9.92 The vapor pressures of pure benzene and pure toluene at 298 K are 94.6 and 29.1 torr, respectively. If 5.00 g each of benzene and toluene are placed in an evacuated container with a volume of 5.0 L and allowed to reach equilibrium, what fraction of the mixture will be in the liquid phase? What is the final pressure? Describe any assumptions that you make.

- 9.93** Two beakers, 1 and 2, containing 50 mL of 0.10 M urea and 50 mL of 0.20 M urea, respectively, are placed under a tightly sealed container at 298 K. Calculate the mole fraction of urea in the solutions at equilibrium. Assume ideal behavior. Urea is a nonvolatile compound.
- 9.94** Two miscible liquids A and B have vapor pressures of 123 mmHg and 564 mmHg at 25°C, respectively, when pure. If 1.4 moles of A are mixed with an unknown amount of B, the resulting solution has a vapor pressure of 427 mmHg at 25°C. Determine the amount of B that was added to form this solution.
- 9.95** At 298 K, the osmotic pressure of a glucose solution is 10.50 atm. Calculate the freezing point of the solution. The density of the solution is 1.16 g mL $^{-1}$.
- 9.96** A closed vessel of volume 9.6 L contains 2.0 g of water. Calculate the temperature (in °C) at which half of the water is in the vapor phase and half is liquid.
- 9.97** The normal boiling point of methanol is 65.0°C, and the standard enthalpy of formation of methanol vapor is $-202.2\text{ kJ mol}^{-1}$. Calculate the vapor pressure of methanol (in mmHg) at 25°C. (*Hint:* See Appendix 2 for other thermodynamic data of methanol.)
- 9.98** Henry's law constants for the noble gases in water are listed in Table 9.2. Do these values exhibit a trend with increasing atomic number? If so, give an explanation for this trend in terms of intermolecular forces.
- 9.99** Using Equations 9.21 and 9.24 and data from Tables 7.7 and 7.8, calculate the freezing-point depression and boiling-point elevation constants for diethyl ether.
- 9.100** In Example 9.3, we used data for the vapor pressure of water at several temperatures to estimate the molar enthalpy of vaporization of water. In this example, the pressures were in units of mmHg. The numerical values of P (and thus $\ln P$) will depend upon the choice of units; however, the calculated molar enthalpy of vaporization should be independent of this choice. (a) Convert the pressure values in Example 9.3 to bar and repeat the calculation of ΔH_{vap} for water to demonstrate that the value obtained does not depend upon the pressure units. (b) Demonstrate mathematically that the slope of Equation 9.5 (and thus ΔH_{vap}) is independent of the units used for pressure.

Answers to Practice Exercises

9.1 -37.6°C **9.2** 369 mmHg **9.3** 61.3 kJ mol^{-1} [This is the average over the temperature range 323 K to 433 K, and therefore, it differs slightly from the value of 59.0 given in Table 7.7, which is measured at the boiling point of Hg (630 K)].

9.4 CS₂ **9.5** $2.9 \times 10^{-4}\text{ mol L}^{-1}$ **9.6** (a) 85 torr; (b) for benzene 0.654, for heptane 0.346 **9.7** 37.8 mmHg; 4.4 mmHg **9.8** T_b : 101.3°C; T_f : -4.48°C **9.9** 21.3 bar **9.10** 0.066 m ; $1.3 \times 10^2\text{ g mol}^{-1}$ **9.11** $2.60 \times 10^4\text{ g}$ **9.12** 1.21

10

Chapter

Chemical Equilibrium



When a chemical reaction has reached the equilibrium state, the concentrations of reactants and products remain constant over time, and there are no visible changes in the system. However, there is much activity at the molecular level because reactant molecules continue to form product molecules while product molecules react to yield reactant molecules. This dynamic process is the subject of this chapter. We will discuss different types of equilibrium reactions, the meaning of the equilibrium constant and its relationship to thermodynamics, and how chemical equilibrium shifts in response to changes in external conditions.

10.1 The Equilibrium Constant Governs the Concentration of Reactants and Products at Equilibrium 512

10.2 The Equilibrium Constant Can Be Used to Predict the Direction and Equilibrium Concentrations of a Chemical Reaction 524

10.3 The Equilibrium Constant for a Reaction Can Be Determined from the Standard Gibbs Energy Change 531

10.4 The Response of an Equilibrium System to a Change in Conditions Can Be Determined Using Le Châtelier's Principle 536

10.1 | The Equilibrium Constant Governs the Concentration of Reactants and Products at Equilibrium

Few chemical reactions proceed in only one direction. Most are, at least to some extent, **reversible reactions**, that is, *they can proceed in either the forward or reverse direction*. At the start of a reversible reaction, the reaction proceeds toward the formation of products. As soon as some product molecules are formed, the reverse reaction begins to take place and reactant molecules are formed from product molecules. Eventually, the rates of product and reactant formation will equalize, and the system will have attained a state of *chemical equilibrium in which the concentrations of the reactants and products no longer change*. Like physical equilibrium (discussed in Chapters 5 and 8), chemical equilibrium is a dynamic process. However, the transformations involved in chemical equilibrium require the breaking and formation of chemical bonds, whereas physical equilibrium involves the transfer of intact molecules between different physical phases of a substance and no chemical bonds are broken in the process.



NO_2 and N_2O_4 gases at equilibrium.

The reversible reaction between dinitrogen tetroxide (N_2O_4) and nitrogen dioxide (NO_2), depicted with space-filling models in Figure 10.1, is an example of a chemical equilibrium. The progress of the reaction



can be monitored easily because N_2O_4 is a colorless gas, whereas NO_2 , a component of smog, has a dark brown color. (The reaction is written with a double arrow to show that it is a reversible reaction.) Suppose that N_2O_4 is injected into an evacuated flask. Some brown color appears immediately, indicating the formation of NO_2 molecules. The color intensifies as the dissociation of N_2O_4 continues until eventually an equilibrium is reached. Beyond that point, no further change in color is evident because the partial pressures (and, by Dalton's law, the concentrations) of both N_2O_4 and NO_2 remain constant. Individual molecules of N_2O_4 continue to dissociate into NO_2 molecules, and individual NO_2 molecules continue to combine to form N_2O_4 molecules, but the net concentrations of reactants and products does not change once equilibrium is established.

An equilibrium state can also be established by starting with pure NO_2 . As NO_2 molecules combine to form N_2O_4 , the color fades. The color never completely disappears, though, because some of the newly formed N_2O_4 molecules dissociate into NO_2 molecules again. Yet another way to create an equilibrium state is to start with a mixture of NO_2 and N_2O_4 and monitor the system until the color stops changing. These studies demonstrate that the reaction between N_2O_4 and NO_2 is indeed reversible, because a pure component (N_2O_4 or NO_2) reacts to give the other gas. The important thing to keep in mind is that at equilibrium, the conversions of N_2O_4 to

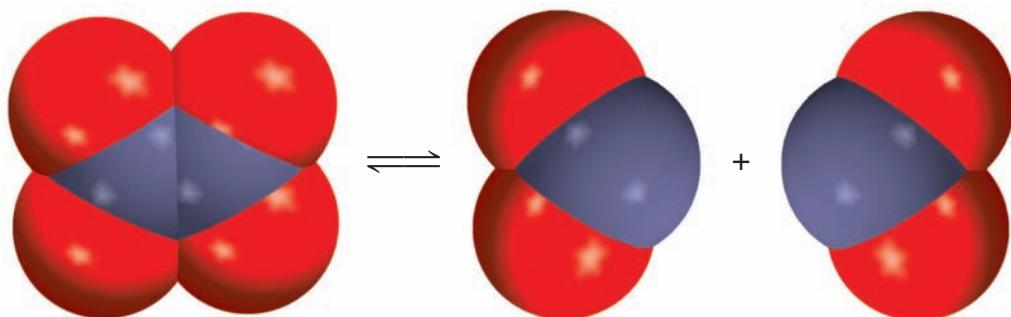


Figure 10.1 Space-filling models depicting the reversible reaction between N_2O_4 and NO_2 molecules.

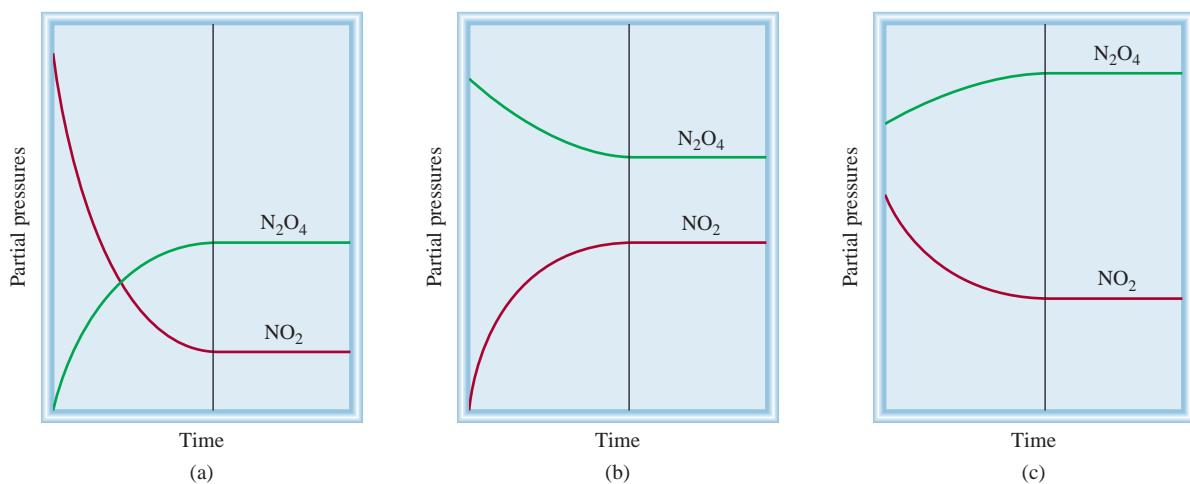


Figure 10.2 Graphs showing the change in the partial pressures of NO_2 and N_2O_4 with time, beginning with three different initial partial pressures of reactants and products. (a) Initially only NO_2 is present. (b) Initially only N_2O_4 is present. (c) Initially a mixture of NO_2 and N_2O_4 is present. Even though equilibrium is reached in all three cases, the equilibrium partial pressures of NO_2 and N_2O_4 are not the same.

NO_2 and of NO_2 to N_2O_4 are still going on. We do not see a color change because the two rates are equal—the removal of NO_2 molecules takes place as fast as the production of NO_2 molecules, and N_2O_4 molecules are formed as quickly as they dissociate. The graphs in Figure 10.2 summarize these three situations.

The Equilibrium Constant

Table 10.1 lists some experimental data for the $\text{NO}_2\text{-N}_2\text{O}_4$ system at 25°C . The gas concentrations are expressed as partial pressures, which can be calculated at a given temperature (using the ideal gas law) from the number of moles of the gases present initially and at equilibrium and the volume of the flask in liters. The last two columns of Table 10.1 use the equilibrium data to compare the ratios of $P_{\text{NO}_2}/P_{\text{N}_2\text{O}_4}$ and $P_{\text{NO}_2}^2/P_{\text{N}_2\text{O}_4}$, where pressures are measured in bar. Although the ratio $P_{\text{NO}_2}/P_{\text{N}_2\text{O}_4}$ gives scattered values, the ratio $P_{\text{NO}_2}^2/P_{\text{N}_2\text{O}_4}$ gives a nearly constant value that averages 0.115:

$$K = \frac{(P_{\text{NO}_2}/P^\circ)^2}{(P_{\text{N}_2\text{O}_4}/P^\circ)} = 0.115 \quad (10.1)$$

where K is a constant for the equilibrium reaction $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ at 25°C . (To make K unitless, we have divided each partial pressure in Equation 10.1 by the standard pressure $P^\circ = 1$ bar.) The exponent 2 for P_{NO_2} in this expression is the same as the stoichiometric coefficient for NO_2 in the reversible reaction.

Equation 10.1 is an example of the **law of mass action**, which holds that *for a reversible reaction at equilibrium and at a constant temperature, a certain ratio of reactant and product concentrations has a constant value K (called the equilibrium constant)*. This law was first formulated by two Norwegian chemists, Cato Guldberg¹ and Peter Waage,² in 1864.

1. Cato Maximilian Guldberg (1836–1902). Norwegian chemist and mathematician. Guldberg's research was mainly in thermodynamics.

2. Peter Waage (1833–1900). Norwegian chemist. Like that of his coworker, Guldberg, Waage's research was primarily in thermodynamics.

Table 10.1 NO₂-N₂O₄ System at 25°C

| Initial Partial Pressures (bar) | Equilibrium Partial Pressures (bar) | | Ratio of Partial Pressures at Equilibrium | |
|---------------------------------|---|-----------------------------|---|--|
| P _{NO₂} | P _{N₂O₄} | P _{NO₂} | P _{N₂O₄} | P _{NO₂} /P _{N₂O₄} |
| 0.000 | 16.60 | 1.355 | 15.93 | 0.0851 |
| 1.238 | 11.05 | 1.132 | 11.10 | 0.102 |
| 0.7433 | 12.39 | 1.177 | 12.16 | 0.0968 |
| 0.9910 | 14.86 | 1.296 | 14.72 | 0.0880 |
| 4.955 | 0.000 | 0.5054 | 2.225 | 0.227 |

The law of mass action can be generalized in its modern form for the following reversible reaction:



where b , c , d , and e are stoichiometric coefficients. For this reaction at equilibrium at a particular temperature,

$$K = \frac{a_D^d a_E^e}{a_B^b a_C^c} \quad (10.2)$$

where a_i is called the **activity** of component i . The activity of a species in a reaction is generally a complex function of the pressures and concentrations of all the components present in the reaction mixture. In many very important cases, however, the activity of a species takes on a simple form:

- **Ideal gases:** Gases at low to moderate pressures (less than a few bar) behave ideally, at least to a good approximation. The activity of an ideal gas of species i is given by its partial pressure in units of the standard pressure $P^\circ = 1$ bar:

$$a_i = \frac{P_i}{P^\circ} \quad (\text{ideal gas}) \quad (10.3)$$

We will often omit the P° from equilibrium constant expressions involving gases and write $a_i = P_i$, with the understanding that P_i is a dimensionless quantity numerically equal to the partial pressure in bar.

- **Solutes in dilute solution:** A solute present in a solution in dilute concentrations will exhibit nearly ideal solution behavior. Here “dilute” is typically taken to be less than 0.1 M for nonelectrolyte solutions and less than 0.01 M for electrolyte solutions. The activity of a solute i in an ideal solution is given by its molarity relative to the standard-state concentration $c^\circ = 1$ mol L⁻¹:

$$a_i = \frac{[i]}{c^\circ} \quad (\text{dilute solute}) \quad (10.4)$$

We will often omit the c° from equilibrium constant expressions involving solutes and write $a_i = [i]$, with the understanding that $[i]$ is a dimensionless quantity numerically equal to the molarity.

- **Pure solids and liquids:** The activity of a pure (or nearly pure) solid or liquid in a reaction can be well approximated by assuming that

$$a_i = 1 \quad (\text{pure solid or liquid}) \quad (10.5)$$

The activity of a species is a dimensionless quantity, so the equilibrium constant K is dimensionless, too.

Both the partial pressure of an ideal gas and the molarity of a solute are measures of the concentration of a material in a reaction mixture, so the activity can be viewed as a measure of the effective amount of a substance available for reaction. At high gas pressures or high solute concentrations, the activities of reacting species may differ somewhat from the expressions in Equations 10.3 and 10.4 due to the influence of strong intermolecular interactions. For the purposes of the most of the reactions considered in this book, however, using Equations 10.3 to 10.5 will be sufficient to describe equilibrium. An example where the deviation from ideal solution behavior is important was discussed in Section 9.4, where it was necessary to use nonintegral values of the van't Hoff factor to compensate for ion pairing in determining the colligative properties of electrolyte solutions. The presence of ion pairing decreases the effective number of solute particles in solution; in other words, the activity of the solute is smaller than the numerical value of the solute molarity.

The validity of the law of mass action (illustrated by Equation 10.2) has been established by studying many reversible reactions. The equilibrium constant, then, is defined by a *quotient*. The numerator of the quotient is obtained by multiplying together the equilibrium activities of the *products*, each raised to a power equal to its stoichiometric coefficient in the balanced equation. The denominator of the quotient is obtained by multiplying together the equilibrium activities of the *reactants*, each raised to a power equal to its stoichiometric coefficient in the balanced equation. As will be discussed in Section 10.3, the form of the equilibrium constant, as well as the specific value of K for a given reaction, can be determined from thermodynamics.

The magnitude of the equilibrium constant indicates whether an equilibrium reaction favors the products or the reactants. If K is much greater than 1 (i.e., $K \gg 1$), the equilibrium lies to the right and favors the products. Conversely, if the equilibrium constant is much smaller than 1 (i.e., $K \ll 1$), the equilibrium lies to the left and favors the reactants. In this context, any number greater than 10 is considered to be much greater than 1, and any number less than 0.1 is much less than 1.

The signs \ll and \gg mean "much less than" and "much greater than," respectively.

Although the law of mass action and the equilibrium constant can be used to predict the amounts of reactants and products that are present in the system when equilibrium is established, these concepts have no bearing on the *kinetics* of the reaction, that is, how long it takes a reaction to reach equilibrium. The kinetics of chemical reactions are discussed in Chapter 13.

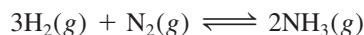
Writing Equilibrium Constant Expressions

Equilibrium constants are the key to solving a wide variety of stoichiometry problems involving equilibrium systems. For example, an industrial chemist who wants to maximize the yield of sulfuric acid must have a clear understanding of the equilibrium constants for all the steps in the process, starting from the oxidation of sulfur and ending with the formation of H_2SO_4 . A physician specializing in clinical cases of acid-base imbalance needs to know the equilibrium constants of weak acids and bases. And, knowledge of equilibrium constants of pertinent gas-phase reactions will help an atmospheric chemist better understand the process of ozone destruction in the stratosphere.

To use equilibrium constants, we must express them in terms of the reactant and product concentrations. Our only guide is the law of mass action (Equation 10.2), which is the general formula for finding equilibrium activities in terms of the equilibrium constant, and the expressions for the relationship of activities to concentrations (or partial pressures) given by Equations 10.3 to 10.5. Because the concentrations of the reactants and products can often be expressed in different ways, however, and because the reacting species are not always in the same phase, there may be more than one way to express the equilibrium constant for the *same* reaction. To begin with, we will consider reactions in which the reactants and products are in the same phase.

Homogeneous Equilibria

Homogeneous equilibria are equilibrium reactions in which all reacting species are in the same phase. The gas-phase equilibrium between NO_2 and N_2O_4 is a homogeneous equilibrium as is the reaction of hydrogen with nitrogen to form ammonia:

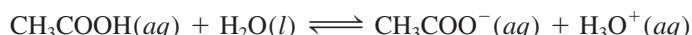


The equilibrium constant, as given in Equation 10.2, is

$$K = \frac{a_{\text{NH}_3}^2}{a_{\text{H}_2}^3 a_{\text{N}_2}} = \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 P_{\text{N}_2}}$$

where we have assumed ideal gas behavior for the activities (Equation 10.3 with the P° term omitted for simplicity).

The ionization of acetic acid (CH_3COOH) in water is a homogeneous equilibrium:



The equilibrium constant expression is

$$K = \frac{a_{\text{CH}_3\text{COO}^-(aq)} a_{\text{H}_3\text{O}^+(aq)}}{a_{\text{CH}_3\text{COOH}(aq)} a_{\text{H}_2\text{O}(l)}} = \frac{[\text{CH}_3\text{COO}^-(aq)][\text{H}_3\text{O}^+(aq)]}{[\text{CH}_3\text{COOH}(aq)]}$$

where we have assumed that the solutes $\text{CH}_3\text{COOH}(aq)$, $\text{CH}_3\text{COO}^-(aq)$, and $\text{H}_3\text{O}^+(aq)$ are sufficiently dilute that their activities can be expressed as solute molarities. $\text{H}_2\text{O}(l)$ represents a nearly pure liquid in this system, so its activity is equal to unity and it does not appear in the final equilibrium expression.

Example 10.1 shows how to write equilibrium constant expressions for homogeneous reactions.

Example 10.1

Write appropriate expressions for K for the following reversible homogeneous reactions at equilibrium:

- $\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)$
- $2\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g)$
- $\text{CH}_3\text{COOH}(aq) + \text{C}_2\text{H}_5\text{OH}(aq) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(aq) + \text{H}_2\text{O}(l)$

Strategy Use the law of mass action (Equation 10.2) to obtain the form of K , and then use Equations 10.3, 10.4, and/or 10.5 to obtain the appropriate expressions for the

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activities, depending upon whether the reactants and products are gases, dilute solutes, or nearly pure liquids.

Solution (a) Equation 10.2 gives

$$K = \frac{a_{F^-(aq)} a_{H_3O^+(aq)}}{a_{HF(aq)} a_{H_2O(l)}} = \frac{[F^-(aq)][H_3O^+(aq)]}{[HF(aq)]}$$

where we have assumed that the concentrations of HF, F^- , and H_3O^+ are dilute enough that the dilute solute expression for the activity (Equation 10.4) holds.

H_2O is the solvent, so it can be treated as a nearly pure liquid in a dilute solution, giving $a_{H_2O} = 1$ (Equation 10.5).

- (b) All of the reacting species are in the gas phase, so the activities can be equated to the partial pressures (as long as the pressures are sufficiently low that the ideal gas law holds).

$$K = \frac{a_{NO_2}^2}{a_{NO}^2 a_{O_2}} = \frac{P_{NO_2}^2}{P_{NO}^2 P_{O_2}}$$

- (c) All of the reacting species are either solutes or a nearly pure solvent (water). From Equations 10.2 and 10.4, the equilibrium constant K is given by

$$K = \frac{a_{CH_3COOC_2H_5(aq)} a_{H_2O(l)}}{a_{CH_3COOH(aq)} a_{C_2H_5OH(aq)}} = \frac{[CH_3COOC_2H_5(aq)]}{[CH_3COOH(aq)][C_2H_5OH(aq)]}$$

Practice Exercise Write K for

- (a) the decomposition of nitrogen pentoxide:



Sometimes it is convenient to express the equilibrium constant for a reaction in terms of alternate units. Consider, for example, the following generalized equilibrium in the gas phase:



where a and b are stoichiometric coefficients. The equilibrium constant K , assuming ideal gas behavior, is given by

$$K = \frac{P_B^b}{P_A^a}$$

Suppose that it is easier to measure the concentration (in mol L⁻¹) than it is the pressure. We can convert the partial pressure of A in this expression to molarity using the ideal gas law:

$$\begin{aligned} P_A V &= n_A RT \\ P_A &= \frac{n_A}{V} RT = [A]RT \end{aligned}$$

where $[A]$ is the molarity of A. Similarly, for B, we have $P_B = [B]RT$. Substituting into the expression for K gives

$$K_P = \frac{P_B^b}{P_A^a} = \frac{([B]RT)^b}{([A]RT)^a} = \frac{[B]^b}{[A]^a} \times (RT)^{b-a}$$

where we have used the subscript “P” in the equilibrium constant to indicate specifically that the gas activities are measured as partial pressures, not concentrations. The **concentration equilibrium constant** for this reaction, K_c , can be defined as

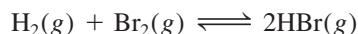
$$K_c = \frac{[B]^b}{[A]^a}$$

The two equilibrium constant expressions are related by

$$K_P = K_c(RT)^{\Delta n} \quad (10.6)$$

where $\Delta n = b - a = \text{moles of gaseous products} - \text{moles of gaseous reactants}$.

In general, $K_P \neq K_c$ except in the special case in which $\Delta n = 0$ as in the equilibrium mixture of molecular hydrogen, molecular bromine, and hydrogen bromide:



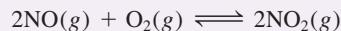
In this case, Equation 10.6 can be written as

$$K_P = K_c(RT)^0 = K_c$$

Example 10.2 shows how to calculate K_P and K_c from a specific reaction.

Example 10.2

The following equilibrium process has been studied at 230°C:



In one experiment the concentrations of the reacting species at equilibrium were found to be $[\text{NO}] = 2.71 \times 10^{-3} M$, $[\text{O}_2] = 0.127 M$, and $[\text{NO}_2] = 0.775 M$. Calculate the equilibrium constants K_c and K_P for this reaction at 230°C.

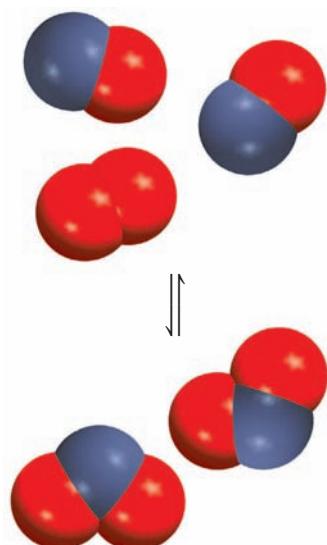
Strategy The concentrations given are equilibrium concentrations. They have units of mol L^{-1} , so we can calculate the concentration equilibrium constant K_c as a ratio of molarities. The equilibrium constant K_P can be calculated from the value of K_c using Equation 10.6 with $\Delta n = 2 - (2 + 1) = -1$.

Solution The concentration equilibrium constant is given by

$$K_c = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]}$$

where the concentrations are in M . Substituting the concentrations, we find that

$$K_c = \frac{(0.775)^2}{(2.71 \times 10^{-3})^2(0.127)} = 6.44 \times 10^5$$



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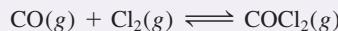
For K_P we use Equation 10.6:

$$K_P = K_c (RT)^{\Delta n} = (6.44 \times 10^5) [(0.08314)(503)]^{-1} = 1.54 \times 10^4$$

We must use the gas constant ($R = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$) and the temperature (503 K) without units so that K_P will remain dimensionless.

Check The large magnitudes of K_c and K_P are consistent with the high product (NO_2) concentration relative to the concentrations of the reactants (NO and O_2).

Practice Exercise Carbonyl chloride (COCl_2), also called phosgene, was used in World War I as a poisonous gas. The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form carbonyl chloride,



at 74°C are $[\text{CO}] = 1.2 \times 10^{-3} M$, $[\text{Cl}_2] = 0.054 M$, and $[\text{COCl}_2] = 0.14 M$. Calculate the equilibrium constants K_c and K_P .

Heterogeneous Equilibrium

Heterogeneous equilibria are equilibrium reactions in which the reactants and products are in different phases. When solid calcium carbonate is heated in a closed vessel, for example, the following equilibrium is attained:



The two solids and one gas constitute three separate phases. At equilibrium, the equilibrium constant expression can be written as

$$K = \frac{a_{\text{CaO}(s)} a_{\text{CO}_2(g)}}{a_{\text{CaCO}_3(s)}}$$

According to Equation 10.5, the activities of the pure solids (CaO and CaCO_3) are equal to unity. According to Equation 10.3, the activity for the gas (CO_2) is given by the numerical value of its partial pressure in bar, thus,

$$K = \frac{1 \times P_{\text{CO}_2}}{1} = P_{\text{CO}_2}$$

The equilibrium constant in this case is numerically equal to the pressure of CO_2 gas in bar, which is an easily measurable quantity. In other words, the value of the equilibrium constant is independent of the amount of CaCO_3 or CaO that is present, as long as some of each is present at equilibrium (Figure 10.3).

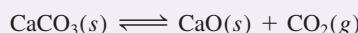
Example 10.3 illustrates the calculation of equilibrium constants for a heterogeneous reaction.



The mineral calcite is made of calcium carbonate, as are chalk and marble.

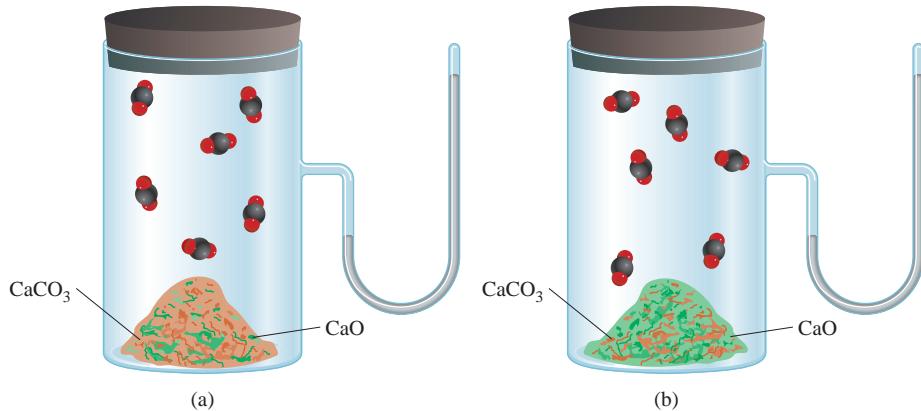
Example 10.3

Consider the heterogeneous equilibrium shown in Figure 10.3:



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Figure 10.3 The equilibrium pressure of CO_2 is the same in (a) and (b) at the same temperature, despite the presence of different amounts of CaCO_3 (shown in brown) and CaO (shown in green).



Continued—

At 800°C , the pressure of CO_2 is 0.239 bar. Calculate (a) K_P and (b) K_c for the reaction at this temperature.

Strategy Remember that the activity of pure solids can be well approximated as 1, so concentrations of pure solids will not appear in the final equilibrium constant expression. The relationship between K_P and K_c is given by Equation 10.6

Solution (a) Using Equation 10.2 we have

$$K = \frac{a_{\text{CaO}(s)} a_{\text{CO}_2(g)}}{a_{\text{CaCO}_3(s)}}$$

Using Equations 10.3 and 10.5 to approximate the activities gives

$$K_P = \frac{1 \times P_{\text{CO}_2}}{1} = P_{\text{CO}_2} = 0.239$$

where again we have used the subscript “P” to specifically indicate that partial pressures are being used for the gas phase activities.

(b) From Equation 10.6, we know

$$K_P = K_c (RT)^{\Delta n}$$

In this case, $T = 800 + 273 = 1073$ K and $\Delta n = 1$, so we substitute these values in the equation and obtain

$$\begin{aligned} 0.239 &= K_c (0.08314 \times 1073) \\ K_c &= 2.68 \times 10^{-3} \end{aligned}$$

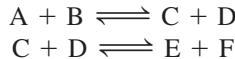
Practice Exercise Consider the following equilibrium at 395 K:



The partial pressure of each gas is 0.268 bar. Calculate K_P and K_c for the reaction.

Multiple Equilibria

The reactions we have considered so far are all relatively simple. A more complicated case is one in which the product molecules from one equilibrium system are involved in a second equilibrium process. Consider the following pair of gas-phase equilibria:



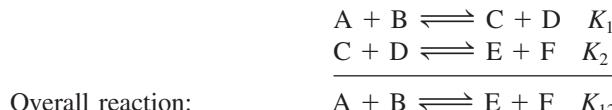
The products formed in the first reaction, C and D, react further to form products E and F. At equilibrium we can write two separate equilibrium constants:

$$K_1 = \frac{P_{\text{C}}P_{\text{D}}}{P_{\text{A}}P_{\text{B}}}$$

and

$$K_2 = \frac{P_{\text{E}}P_{\text{F}}}{P_{\text{C}}P_{\text{D}}}$$

The overall reaction is given by the sum of the two reactions



and the equilibrium constant K for the overall reaction is

$$K_{12} = \frac{P_{\text{E}}P_{\text{F}}}{P_{\text{A}}P_{\text{B}}}$$

We obtain the same expression if we take the product of the expressions for K_1 and K_2

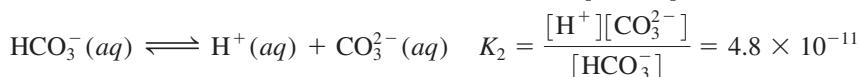
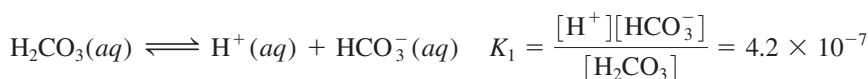
$$K_1 \times K_2 = \frac{P_{\text{C}}P_{\text{D}}}{P_{\text{A}}P_{\text{B}}} \times \frac{P_{\text{E}}P_{\text{F}}}{P_{\text{C}}P_{\text{D}}} = \frac{P_{\text{E}}P_{\text{F}}}{P_{\text{A}}P_{\text{B}}}$$

Therefore,

$$K_{12} = K_1 K_2 \quad (10.7)$$

We can now make an important statement about multiple equilibria: *If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants for the individual reactions.*

Among the many known examples of multiple equilibria is the ionization of diprotic acids in aqueous solution. The following equilibrium constants have been determined for carbonic acid (H_2CO_3) at 25°C:



The overall reaction is the sum of these two reactions



and the corresponding equilibrium constant is given by

$$K = \frac{[\text{H}^+]^2[\text{CO}_3^{2-}]}{[\text{H}_2\text{CO}_3]}$$

Using Equation 10.7,

$$K = K_1 K_2 = (4.2 \times 10^{-7})(4.8 \times 10^{-11}) = 2.0 \times 10^{-17}$$

The Form of K and the Equilibrium Expression

Besides Equation 10.7, there are two more important rules for writing equilibrium constants:

- When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant. Thus, if we write the $\text{NO}_2\text{-N}_2\text{O}_4$ equilibrium as



then at 25°C

$$K_1 = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = 0.115$$

However, we can represent the equilibrium equally well as

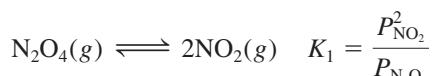
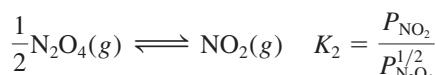


and the equilibrium constant is now given by

$$K_{-1} = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} = 8.70$$

Thus, $K_{-1} = 1/K_1$ or $K_1 \times K_{-1} = 1$. Both K_1 and K_{-1} are valid equilibrium constants, but it is meaningless to say that the equilibrium constant for the $\text{NO}_2\text{-N}_2\text{O}_4$ system is 0.115 or 8.70 unless we also specify how the equilibrium equation is written.

- The value of K also depends upon how the equilibrium equation is balanced. Consider the following ways of describing the same equilibrium:



The second reaction can be obtained by adding the first reaction to itself, so according to Equation 10.7, $K_1 = K_2 \times K_2 = K_2^2$. The equilibrium constant for the second reaction (K_1) was given at the beginning of this section as 0.115 at 25°C, so the equilibrium constant for the first reaction (K_2) can be obtained from the square root of K_1 or 0.339.

According to the law of mass action, each activity term in the equilibrium constant expression is raised to a power equal to its stoichiometric coefficient. Thus, if you double the stoichiometric coefficients in a chemical equation throughout, the corresponding equilibrium constant will be the square of the original value; if you triple the stoichiometric coefficients in a chemical equation, the equilibrium constant will be the cube of the original value, and so on. The NO_2 - N_2O_4 example also demonstrates why you need to write the chemical equation when quoting the numerical value of the equilibrium constant.

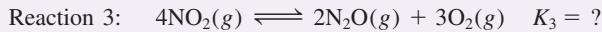
Example 10.4 shows how to use equilibrium constant data from two reactions to calculate the equilibrium constant of a third related reaction.

Example 10.4

Consider the following gas-phase reaction equilibria involving N_2O_4 :

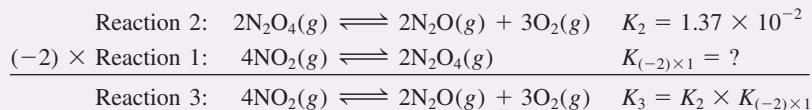


Use this information to determine the equilibrium constant for the following reaction:



Strategy If we can write reaction 3 in terms of reactions 1 and 2, we can use Equation 10.7 and the other two rules for writing equilibrium constants to express K_3 as a function of K_1 and K_2 .

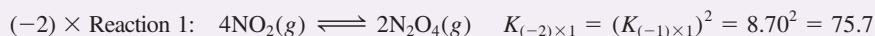
Solution We can write reaction 3 as the sum of reaction 2 and twice the reverse of Reaction 1:



[Here we use the notation $K_{(-2)\times 1}$ to denote the equilibrium constant for the reaction obtained by multiplying reaction 1 by (-2) .] Using Equation 10.7, the equilibrium constant for Reaction 3 is then given by the product of the equilibrium constant for Reaction 2 (K_2) and the equilibrium constant for the reaction that is twice the reverse of Reaction 1 ($K_{(-2)\times 1}$). The equilibrium constant for the reverse of Reaction 1 is the reciprocal of the equilibrium constant for the forward reaction,



and multiplying a reaction through by 2 means that the equilibrium constant must be squared:



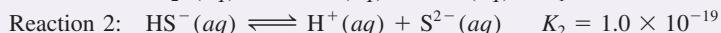
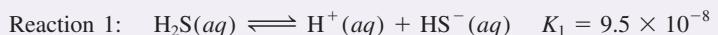
Combining these two equilibrium constants yields K_3 :

$$K_3 = K_2 \times K_{(-2)\times 1} = (1.37 \times 10^{-2})(75.7) = 1.04$$

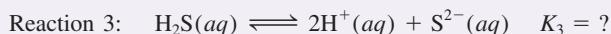
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Practice Exercise The following equilibrium constants have been determined for hydrosulfuric acid at 25°C:



Calculate the equilibrium constant for the following reaction at the same temperature:



Summary of Guidelines for Writing Equilibrium Expressions

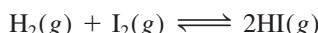
1. The equilibrium constant is written as a ratio of the activities of the products to the activities of the reactants (Equation 10.2). The activities of each species in this ratio are raised to a power equal to the stoichiometric coefficients of the species in the balanced chemical equation.
2. For reactions in which the solute concentrations and partial pressures are low, the gases and solutes are well approximated by ideal gas or ideal solution behavior. For such systems, the activities are given by
 - a. *Ideal gases*: $a_i = P_i/P^\circ$, where P_i = partial pressure of gas i and $P^\circ = 1$ bar.
 - b. *Dilute solutes*: $a_i = [i]/c^\circ$, where $[i]$ = molarity of solute in solution and $c^\circ = 1 \text{ mol L}^{-1}$.
 - c. *Pure or nearly pure solids and liquids*: $a_i = 1$.
3. The equilibrium constant K is a dimensionless quantity.
4. In quoting a value for the equilibrium constant, we must specify the balanced chemical equation and the temperature.
5. If the equilibrium equation is written for a reaction in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.
6. If the equilibrium equation is multiplied through by a factor n , the equilibrium constant for the new equation becomes the original equilibrium constant raised to the power of n .
7. If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

10.2 | The Equilibrium Constant Can Be Used to Predict the Direction and Equilibrium Concentrations of a Chemical Reaction

We saw in Section 10.1 that the equilibrium constant for a given reaction can be calculated from known equilibrium concentrations. Once we know the value of the equilibrium constant, we can use Equation 10.2 to calculate the unknown equilibrium concentrations (keep in mind, though, that the equilibrium constant has a constant value only if the temperature does not change). In general, the equilibrium constant makes it possible to predict the direction in which a reaction mixture will proceed to achieve equilibrium and to calculate the concentrations of reactants and products once equilibrium has been reached. Both of these applications are discussed in this section.

Predicting the Direction of a Reaction

In the gas phase, hydrogen iodide forms from molecular hydrogen and molecular iodine:



The equilibrium constant for this reaction is 54.3 at 430°C. Suppose that in a certain experiment the initial partial pressures of H₂, I₂, and HI are 0.710 bar, 0.427 bar, and 5.78 bar, respectively, at 430°C. Will there be a net reaction to form more H₂ and I₂ or to form more HI? Inserting these initial pressures into the equilibrium constant expression, assuming ideal-gas behavior, we obtain

$$\left(\frac{P_{\text{HI}}^2}{P_{\text{H}_2}P_{\text{I}_2}}\right)_0 = \frac{(5.78)^2}{(0.710)(0.427)} = 110$$

where the subscript 0 indicates that we are using initial partial pressures (before equilibrium is reached). Because the quotient ($P_{\text{HI}}^2/P_{\text{H}_2}P_{\text{I}_2}$)₀ is greater than K , this system is not at equilibrium. Consequently, some of the HI will react to form more H₂ and I₂ (decreasing the value of the quotient). Thus, the net reaction proceeds from right to left to reach equilibrium.

For reactions that have not reached equilibrium, such as the formation of HI just considered, we obtain, not the equilibrium constant, but instead the **reaction quotient (Q)**, which is the quantity obtained when nonequilibrium activities are substituted into the equilibrium constant expression. In this case, the nonequilibrium activities are the initial partial pressures of the reactants and products. To determine the direction in which the net reaction will proceed to achieve equilibrium, we must compare the values of Q and K . The three possible cases are as follows:

- ▶ $Q < K$ The ratio of initial activities of products to reactants is too small. To reach equilibrium, reactants must be converted to products. The system proceeds from left to right (consuming reactants, forming products) to reach equilibrium.
- ▶ $Q = K$ The initial activities are equilibrium activities. The system is at equilibrium.
- ▶ $Q > K$ The ratio of initial activities of products to reactants is too large. To reach equilibrium, products must be converted to reactants. The system proceeds from right to left (consuming products, forming reactants) to reach equilibrium.

Figure 10.4 shows a comparison of K with Q .

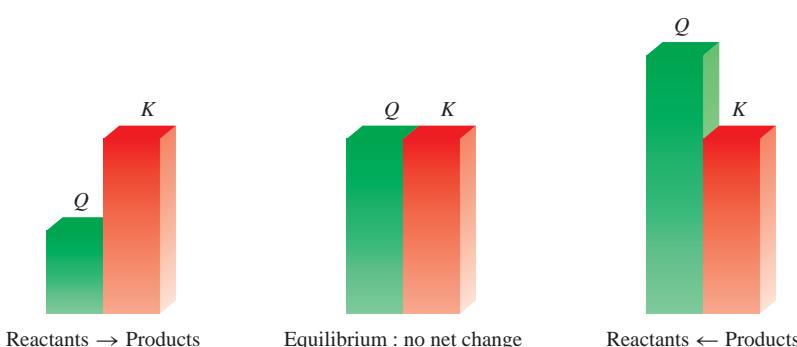
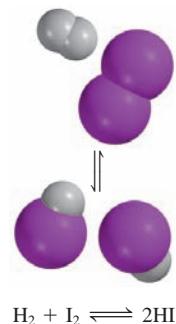
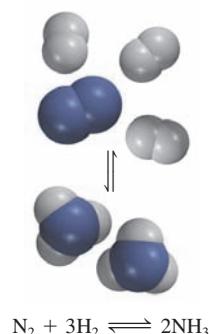


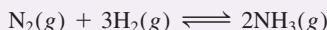
Figure 10.4 The direction of a reversible reaction to reach equilibrium depends on the relative magnitudes of Q and K .

Example 10.5 shows how to use the value of Q to determine the direction of net reaction toward equilibrium.



Example 10.5

At the start of a reaction, there are 0.249 mol N_2 , 3.21×10^{-2} mol H_2 , and 6.42×10^{-4} mol NH_3 in a 3.50-L reaction vessel at 375°C. If the equilibrium constant (K_c) for the reaction



is 1.2 at this temperature, decide whether the system is at equilibrium. If it is not, predict which way the net reaction will proceed to achieve equilibrium.

Strategy The value given for the equilibrium constant is K_c not K_p , so we must use concentrations instead of pressures in the equilibrium expression. The initial amounts of the gases (in moles) in a vessel of known volume (in liters) are given, so we can calculate their molar concentrations and hence the reaction quotient (Q_c). The magnitude of Q_c relative to K_c will indicate the direction of the reaction.

Solution The initial concentrations of the reacting species are

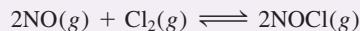
$$\begin{aligned} [\text{N}_2]_0 &= \frac{0.249 \text{ mol}}{3.50 \text{ L}} = 0.0711 \text{ M} \\ [\text{H}_2]_0 &= \frac{3.21 \times 10^{-2} \text{ mol}}{3.50 \text{ L}} = 9.17 \times 10^{-3} \text{ M} \\ [\text{NH}_3]_0 &= \frac{6.42 \times 10^{-4} \text{ mol}}{3.50 \text{ L}} = 1.83 \times 10^{-4} \text{ M} \end{aligned}$$

Next, write the equilibrium constant expression and plug these values into it to obtain Q_c :

$$Q_c = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{(1.83 \times 10^{-4})^2}{(0.0711)(9.17 \times 10^{-3})^3} = 0.611$$

Because $Q_c < K_c$ (1.2), the system is not at equilibrium. The net result will be an increase in the concentration of NH_3 and a decrease in the concentrations of N_2 and H_2 . That is, the net reaction will proceed from left to right until equilibrium is reached.

Practice Exercise Nitrosyl chloride, an orange-yellow compound, forms from nitric oxide and molecular chlorine:



The equilibrium constant (K_c) for this reaction is 6.5×10^4 at 35°C. In a certain experiment, 2.0×10^{-2} mole of NO , 8.3×10^{-3} mole of Cl_2 , and 0.80 moles of NOCl are mixed in a 2.0-L flask. In which direction will the system proceed to reach equilibrium?

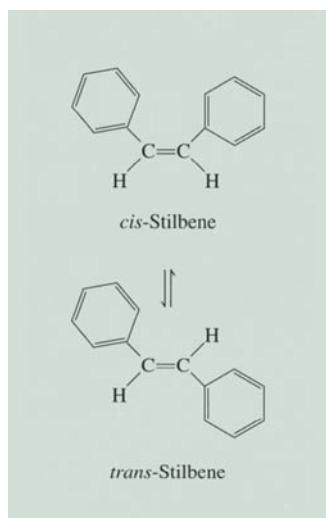


Figure 10.5 The equilibrium between *cis*-stilbene and *trans*-stilbene. Both molecules are geometric isomers, that is, they have the same molecular formula ($\text{C}_{14}\text{H}_{12}$) and the same bond connectivity. In *cis*-stilbene, however, the benzene rings are on one side of the $\text{C}=\text{C}$ double bond and the H atoms are on the other side, whereas in *trans*-stilbene the benzene rings (and the H atoms) are across the $\text{C}=\text{C}$ double bond from each other. *Cis*- and *trans*-stilbene, like most geometric isomers, have different melting points and dipole moments.

Calculating Equilibrium Concentrations

If we know the equilibrium constant for a particular reaction, we can calculate the concentrations in the equilibrium mixture from the initial concentrations. Commonly, only the initial reactant concentrations are given. Consider, for example, the equilibrium between two organic compounds, *cis*-stilbene and *trans*-stilbene, in a nonpolar hydrocarbon solvent (Figure 10.5):



The equilibrium constant (K) for this system is 24.0 at 200°C. Suppose that initially only *cis*-stilbene is present at a concentration of 0.850 mol L⁻¹. How do we calculate the concentrations of *cis*- and *trans*-stilbene at equilibrium? According to the stoichiometry of the balanced chemical equation, 1 mole of *trans*-stilbene forms for every mole of *cis*-stilbene that reacts. If x is the equilibrium concentration of *trans*-stilbene in mol L⁻¹, then the equilibrium concentration of *cis*-stilbene must be $(0.850 - x)$ mol L⁻¹. The changes in concentration can be summarized as follows:

| <i>cis</i> -stilbene \rightleftharpoons <i>trans</i> -stilbene | | |
|--|-------------|------|
| Initial (M): | 0.850 | 0 |
| Change (M): | $-x$ | $+x$ |
| Equilibrium (M): | $0.850 - x$ | x |

A positive (+) change represents an increase and a negative (−) change represents a decrease in concentration at equilibrium. Next, we set up the equilibrium constant expression, substitute the corresponding equilibrium concentrations, and solve for x :

$$K = \frac{[\text{trans-stilbene}]}{[\text{cis-stilbene}]}$$

$$24.0 = \frac{x}{0.850 - x}$$

$$x = 0.816 \text{ M}$$

Having solved for x , we can calculate the equilibrium concentrations of *cis*-stilbene and *trans*-stilbene as follows:

$$[\text{cis-stilbene}] = (0.850 - x) \text{ M} = (0.850 - 0.816) \text{ M} = 0.034 \text{ M}$$

$$[\text{trans-stilbene}] = x \text{ M} = 0.816 \text{ M}$$

Prove to yourself that these results are correct by substituting the calculated values for [cis-stilbene] and [trans-stilbene] back into the equilibrium constant expression and see if you get 24.0, the value given for K .

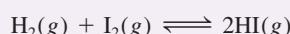
The approach to solving equilibrium constant problems can be summarized as follows:

1. Express the equilibrium concentrations (or partial pressures for gases) of all species in terms of the initial concentrations and a single unknown x , which represents the change in concentration.
2. Write the equilibrium constant expression in terms of the equilibrium concentrations (or partial pressures). Knowing the value of the equilibrium constant, solve for x .
3. Having solved for x , calculate the equilibrium concentrations of all species.

Example 10.6 shows how to apply this three-step procedure to equilibrium problems.

Example 10.6

A mixture of 0.0623 mol H₂, 0.0414 mol I₂, and 0.224 mol HI was placed in a 10.00-L stainless-steel flask at 430°C. The equilibrium constant K_P for the reaction,



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Continued—

is 54.3 at this temperature. Is this system at equilibrium? If not, determine the direction of the reaction and calculate the amounts of H₂, I₂, and HI present at equilibrium.

Strategy From the initial amounts of each species and the volume, we can use the ideal gas law to determine the initial pressures. From these initial pressures, we can calculate the reaction quotient (Q_P) to see if the system is already at equilibrium or, if not, in which direction the net reaction will proceed to reach equilibrium. If the system is not in equilibrium, we must use the equilibrium constant given and the procedure above to determine the equilibrium amounts.

Solution First we need to find the initial partial pressures using the ideal gas law:

$$P_i = n_i \frac{RT}{V}$$

For this temperature and volume, $RT/V = (0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(703.15 \text{ K})/(10.0 \text{ L}) = 5.846 \text{ bar mol}^{-1}$, so

$$(P_{\text{H}_2})_0 = (0.0623 \text{ mol})(5.846 \text{ bar mol}^{-1}) = 0.364 \text{ bar}$$

$$(P_{\text{I}_2})_0 = (0.0414 \text{ mol})(5.846 \text{ bar mol}^{-1}) = 0.242 \text{ bar}$$

$$(P_{\text{HI}})_0 = (0.224 \text{ mol})(5.846 \text{ bar mol}^{-1}) = 1.31 \text{ bar}$$

Substituting the initial partial pressures into the appropriate reaction quotient expression gives

$$Q_P = \frac{(P_{\text{HI}})_0^2}{(P_{\text{H}_2})_0(P_{\text{I}_2})_0} = \frac{(1.31)^2}{(0.364)(0.242)} = 19.5$$

Because Q_P (19.5) is smaller than K_P (54.3), we conclude that the net reaction will proceed from left to right until equilibrium is reached (see Figure 10.4), that is, there will be a depletion of H₂ and I₂ and a gain in HI.

We can now use the three-step procedure to calculate the equilibrium concentrations.

Step 1: The stoichiometry of the reaction is 1 mol H₂ reacting with 1 mol I₂ to yield 2 mol HI. Let x be the depletion in pressure (in bar) of H₂ and I₂ at equilibrium. Based on the stoichiometry of the balanced chemical equation, then, the change in the equilibrium partial pressure of HI must be $2x$. The changes in concentrations can be summarized as follows:

| | H ₂ (g) | + | I ₂ (g) | ↔ | 2HI(g) |
|--------------------|--------------------|---|--------------------|---|-------------|
| Initial (bar): | 0.364 | | 0.242 | | 1.31 |
| Change (bar): | $-x$ | | $-x$ | | $+2x$ |
| Equilibrium (bar): | $0.364 - x$ | | $0.242 - x$ | | $1.31 + 2x$ |

Step 2: The equilibrium constant is given by

$$K_P = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} P_{\text{I}_2}}$$

Substituting, we get

$$K_P = \frac{(1.31 + 2x)^2}{(0.364 - x)(0.242 - x)} = 54.3$$

To solve this equation, we begin by clearing the denominator to give

$$(1.31 + 2x)^2 = (54.3)(0.364 - x)(0.242 - x)$$

$$1.72 + 5.24x + 4x^2 = 4.78 - 32.9x + 54.3x^2$$

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Grouping like terms, we get

$$50.3x^2 - 38.1x + 3.06 = 0$$

This is a quadratic equation of the form $ax^2 + bx + c = 0$. The solution for a quadratic equation (see Appendix 1) is

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

Here we have $a = 50.3$, $b = -38.1$, and $c = 3.06$, so

$$x = 0.0913 \text{ bar} \quad \text{or} \quad x = 0.666 \text{ bar}$$

The second solution is physically impossible because the amounts of H_2 and I_2 reacted would be more than those originally present. The first solution gives the correct answer. When solving quadratic equations of this type, one answer is always physically impossible, so choosing a value for x is relatively straightforward.

Step 3: At equilibrium, the partial pressures are

$$P_{\text{H}_2} = (0.364 - 0.0913) \text{ bar} = 0.273 \text{ bar}$$

$$P_{\text{I}_2} = (0.242 - 0.0913) \text{ bar} = 0.151 \text{ bar}$$

$$P_{\text{HI}} = (1.31 + 2 \times 0.0913) \text{ bar} = 1.49 \text{ bar}$$

The amounts of each gas present at equilibrium can be calculated using the ideal gas law in the form

$$n_i = \frac{P_i V}{RT}$$

$$n_{\text{H}_2} = \frac{P_{\text{H}_2} V}{RT} = \frac{(0.273 \text{ bar})(10.0 \text{ L})}{(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(703.15 \text{ K})} = 0.0467 \text{ mol}$$

$$n_{\text{I}_2} = \frac{P_{\text{I}_2} V}{RT} = \frac{(0.151 \text{ bar})(10.0 \text{ L})}{(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(703.15 \text{ K})} = 0.0258 \text{ mol}$$

$$n_{\text{HI}} = \frac{P_{\text{HI}} V}{RT} = \frac{(1.49 \text{ bar})(10.0 \text{ L})}{(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(703.15 \text{ K})} = 0.255 \text{ mol}$$

Check We can check the answers by calculating K_P using the equilibrium pressures. Substituting the calculated equilibrium partial pressures into the equilibrium expression yields a value of K of 53.8, which is very close to the given value of 54.3. The discrepancy here is due to round-off error.

Comment One can alternatively approach this problem using concentrations instead of pressures by first calculating K_c from the given value of K_c using Equation 10.6. For this particular problem, $\Delta n = 0$, so K_c and K_P would be identical.

Practice Exercise At 1280°C, the equilibrium constant (K_c) is 1.1×10^{-3} for the following reaction:



If the initial concentrations are $[\text{Br}_2]_0 = 6.3 \times 10^{-2} \text{ M}$ and $[\text{Br}]_0 = 1.2 \times 10^{-2} \text{ M}$, calculate the concentrations of these species at equilibrium.

Example 10.6 shows that we can calculate the concentrations of all the reacting species at equilibrium if we know the equilibrium constant and the initial

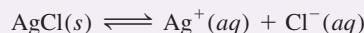
concentrations. This information is valuable if we need to estimate the yield of a reaction.

Suppose, for example, that we started with 0.500 mol of H₂, 0.500 mol of I₂, and no HI in the reaction between H₂ and I₂ to form HI at 430°C. If the reaction were to go to completion, then 2 × 0.500 mol or 1.00 mol HI would form. Because of the equilibrium, however, the actual amount of HI formed when the system reaches equilibrium can be calculated to be 0.786 mol—a 78.6 percent yield.

Example 10.7 gives another example of calculating equilibrium concentrations given the equilibrium constant.

Example 10.7

Consider the following heterogeneous equilibrium:



At 25°C, the equilibrium constant for this reaction is 1.6×10^{-10} . If 5.0 g of AlCl(s) is added to 10.0 L of water initially containing no silver or chloride ions, what will be the equilibrium concentrations of Ag⁺(aq) and Cl⁻(aq) in the solution at this temperature?

Strategy The equilibrium equation contains both ions and a pure solid (AgCl). To set up the equilibrium expression, use Equation 10.2 together with the appropriate approximation for the activities—Equation 10.4 for the ions and Equation 10.5 for AgCl solid.

Solution The equilibrium constant expression (Equation 10.2 together with Equations 10.4 and 10.5) for this equilibrium is

$$K = \frac{a_{\text{Ag}^+} a_{\text{Cl}^-}}{a_{\text{AgCl}(s)}} = [\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10}$$

The equilibrium amounts of Ag⁺ and Cl⁻ will not depend upon the initial amount of AgCl because the amount of solid does not appear in the equilibrium expression (as long as there is a sufficient amount of AgCl so that some is present at equilibrium). Furthermore, from the stoichiometry of the balanced chemical equation, the concentrations of silver ion and chloride ion will be equal because no ions were present in the initial solution and all must come from the dissolution of AgCl. Thus,

$$K = [\text{Ag}^+][\text{Cl}^-] = (x)(x) = x^2 = 1.6 \times 10^{-10}$$

where we have let $x = [\text{Ag}^+] = [\text{Cl}^-]$. Therefore,

$$x = \sqrt{K} = \sqrt{1.6 \times 10^{-10}} = 1.26 \times 10^{-5}$$

The concentrations of Ag⁺ and Cl⁻ in the solution are both $1.26 \times 10^{-5} M$. This concentration is low enough so only a small fraction of the initial amount of solid AgCl will dissolve, and there will be AgCl present at equilibrium.

Comment The equilibrium constant for the dissolution of an ionic compound in aqueous solution is called the *solubility product* and is discussed in more detail in Chapter 12.

Practice Exercise The equilibrium constant K_P is 0.0721 for the following equilibrium at 395 K:



If 20.0 g of ammonium hydrogen sulfide [NH₄HS(s)] is placed in a 10.0 L evacuated container at 395 K, calculate the equilibrium partial pressures of ammonia (NH₃) and hydrogen sulfide (H₂S) and determine the amount of NH₄HS(s) left in the container.

10.3 | The Equilibrium Constant for a Reaction Can Be Determined from the Standard Gibbs Energy Change

In Chapter 7, we learned that the spontaneity of any process under constant pressure and temperature conditions is determined by the sign of ΔG , the change in the Gibbs energy for the process. If $\Delta G < 0$, the process will occur spontaneously; if $\Delta G > 0$, on the other hand, the process will be nonspontaneous. If a system is at a minimum of G , all processes away from that state will be nonspontaneous, so the system will remain at the minimum Gibbs energy state in equilibrium. Thus, all systems in chemical equilibrium represent minima in Gibbs energy relative to changes in the amounts of reactants and products. In this section, we examine the Gibbs energy changes in a reacting system and derive the relationship between the equilibrium constant and the standard Gibbs energy change for a reaction. As was the case for the equations governing binary liquid-vapor equilibria and colligative properties, the mathematical form of the equilibrium constant is a consequence of the Gibbs energy of mixing.

To find the relationship between K and the Gibbs free energy, let's begin with a simple gas-phase reaction:



A sample of pure A gas is placed in the reaction vessel at an initial partial pressure of 1 bar. The reaction will proceed to the right, forming B, until an equilibrium is established. At equilibrium, the system is a mixture of A and B molecules in the gas phase with partial pressures $P_{A,\text{eq}}$ and $P_{B,\text{eq}}$. To determine the equilibrium partial pressures using thermodynamics, we need to determine the values for the partial pressures of A and B that minimize the Gibbs energy.

The total Gibbs energy for the reacting system is the sum of the Gibbs energy for pure A and pure B (namely, G_A° and G_B° , respectively) and the Gibbs energy of mixing the two (ΔG_{mix}):

$$G = n_A G_A^\circ + n_B G_B^\circ + \Delta G_{\text{mix}}$$

Recall from Section 8.5 that the Gibbs energy of mixing for ideal gases was given by Equation 8.37:

$$\Delta G_{\text{mix}} = RT(n_A \ln x_A + n_B \ln x_B)$$

Thus, the total Gibbs energy can be rewritten as follows:

$$G = n_A G_A^\circ + n_B G_B^\circ + RT(n_A \ln x_A + n_B \ln x_B) \quad (10.8)$$

Based on the stoichiometry of the balanced chemical equation, the total number of moles ($n = n_A + n_B$) is fixed throughout the reaction. Dividing Equation 10.8 by n gives

$$G/n = x_A G_A^\circ + x_B G_B^\circ + RT(x_A \ln x_A + x_B \ln x_B)$$

where we have used the relationships $x_A = n_A/n$ and $x_B = n_B/n$. Because $x_A = 1 - x_B$, we can eliminate x_A to give

$$G/n = \underbrace{(1 - x_B)G_A^\circ + x_B G_B^\circ}_{\text{Gibbs free energy for pure substances}} + \underbrace{RT[(1 - x_B)\ln(1 - x_B) + x_B \ln x_B]}_{\text{Gibbs free energy of mixing}} \quad (10.9)$$

For the reaction $A(g) \rightleftharpoons B(g)$, x_B is a measure of the *extent of reaction*, that is, to monitor the reaction from start to finish, it is only necessary to know x_B . If B is the component with the lowest standard Gibbs energy (i.e., $G_B^\circ < G_A^\circ$), then a graph of

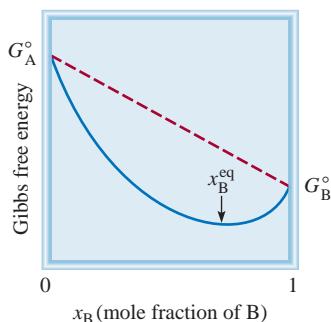


Figure 10.6 Graph of the total Gibbs free energy for the ideal gas reaction $A(g) \rightleftharpoons B(g)$ as a function of x_B , the mole fraction of B, in the reaction mixture (blue line). The red dotted line is the same quantity assuming that there is no Gibbs energy of mixing. The value of x_B corresponding to the minimum in the blue line is the equilibrium composition x_B^{eq} .

Equation 10.9 as a function of x_B will give the blue curve shown in Figure 10.6. The value of x_B at equilibrium (x_B^{eq}) corresponds to the minimum value of G on this curve.

The minimum value of G in Equation 10.9 can be found by finding the value of x_B at which the derivative (slope) of $G(x_B)$ is equal to zero. Taking the derivative of Equation 10.9 gives

$$\begin{aligned}\frac{d(G/n)}{dx_B} &= \frac{d}{dx_B}\{(1 - x_B)G_A^\circ + x_BG_B^\circ + RT[(1 - x_B)\ln(1 - x_B) + x_B\ln x_B]\} \\ &= G_B^\circ - G_A^\circ + RT\ln\frac{x_B}{1 - x_B} \\ \frac{d(G/n)}{dx_B} &= \Delta G_{\text{rxn}}^\circ + RT\ln\left(\frac{x_B}{x_A}\right)\end{aligned}\quad (10.10)$$

where $\Delta G_{\text{rxn}}^\circ = G_B^\circ - G_A^\circ$ is the standard Gibbs free energy of the reaction. For these two gases, the ratio (x_B/x_A) is equal (by Dalton's law) to the ratio of the partial pressures (P_B/P_A), which for this reaction [$A(g) \rightleftharpoons B(g)$] is equal to the reaction quotient.

$$Q = \frac{P_B}{P_A} = \frac{x_B}{x_A}$$

For a given initial value of x_A , the direction in which the reaction will spontaneously proceed depends upon the slope of the curve (dG/dx_B) in Figure 10.6 because the reaction will always proceed in the direction that lowers G . With this in mind, we define

$$\Delta G_{\text{rxn}} \equiv \frac{d(G/n)}{dx_B} = \text{slope of } G \text{ versus extent of reaction curve}$$

Using this definition, Equation 10.10 becomes

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^\circ + RT\ln Q \quad (10.11)$$

Although we have derived Equation 10.11 for the ideal gas-phase reaction $A(g) \rightleftharpoons B(g)$, this result can be shown by thermodynamics to be generally true for all reactions. In short, ΔG_{rxn} depends on two quantities: $\Delta G_{\text{rxn}}^\circ$ and $RT\ln Q$. For a given reaction at temperature T , the value of $\Delta G_{\text{rxn}}^\circ$ is fixed, but that of $RT\ln Q$ is not, because Q varies according to the composition of the reaction mixture. Let us consider two special cases:

Case 1: A large negative value of $\Delta G_{\text{rxn}}^\circ$ will tend to make ΔG_{rxn} negative, too. Thus, the net reaction will proceed from left to right until a significant amount of product has been formed. At that point, the $RT\ln Q$ term will become positive enough to match the negative $\Delta G_{\text{rxn}}^\circ$ term.

Case 2: A large positive $\Delta G_{\text{rxn}}^\circ$ term will tend to make ΔG_{rxn} positive, too. Thus, the net reaction will proceed from right to left until a significant amount of reactant has been formed. At that point, the $RT\ln Q$ term will become negative enough to match the positive $\Delta G_{\text{rxn}}^\circ$ term.

At equilibrium, $\Delta G_{\text{rxn}} = 0$ (the total Gibbs energy is a minimum by definition) and $Q = K$, where K is the equilibrium constant. Thus,

$$0 = \Delta G_{\text{rxn}}^\circ + RT\ln K$$

or

$$\Delta G_{\text{rxn}}^{\circ} = -RT \ln K \quad (10.12)$$

In Equation 10.12, it is important that the quantities that go into making up K are measured relative to the standard states used to determine $\Delta G_{\text{rxn}}^{\circ}$. For gases that means partial pressures in units of bar, and for solutes it means molarity. In a gas-phase reaction, for example, the K in Equation 10.12 refers to K_p , whereas in a reaction in solution it would be K_c . The larger the value of K , the more negative $\Delta G_{\text{rxn}}^{\circ}$ is. For chemists, Equation 10.12 is one of the most important equations in thermodynamics because it enables us to determine the equilibrium constant of a reaction if we know the change in standard free energy and vice versa.

Equation 10.12 relates the equilibrium constant to the *standard* free-energy change ($\Delta G_{\text{rxn}}^{\circ}$) rather than to the *actual* free-energy change (ΔG_{rxn}). The actual free-energy change of the system varies as the reaction progresses and becomes zero at equilibrium. On the other hand, $\Delta G_{\text{rxn}}^{\circ}$ is a constant for a particular reaction at a given temperature. Figure 10.7 shows plots of the free energy of a reacting system versus the extent of the reaction for two types of reactions. Based on the graphs in Figure 10.7 and Equation 10.11,

- ▶ If $\Delta G_{\text{rxn}}^{\circ} < 0$, the products are favored over reactants at equilibrium.
- ▶ If $\Delta G_{\text{rxn}}^{\circ} > 0$, reactants are favored over products at equilibrium.
- ▶ If $\Delta G_{\text{rxn}}^{\circ} = 0$, the system is at equilibrium if all reactants and products are in their standard states.

It is the sign of ΔG_{rxn} , not the sign of $\Delta G_{\text{rxn}}^{\circ}$, that determines the direction of reaction spontaneity. The sign of $\Delta G_{\text{rxn}}^{\circ}$ only tells us the relative amounts of products and reactants when equilibrium is reached, not the direction of the net reaction.

For reactions having very large or very small equilibrium constants, it is generally very difficult, if not impossible, to measure the K values by monitoring the

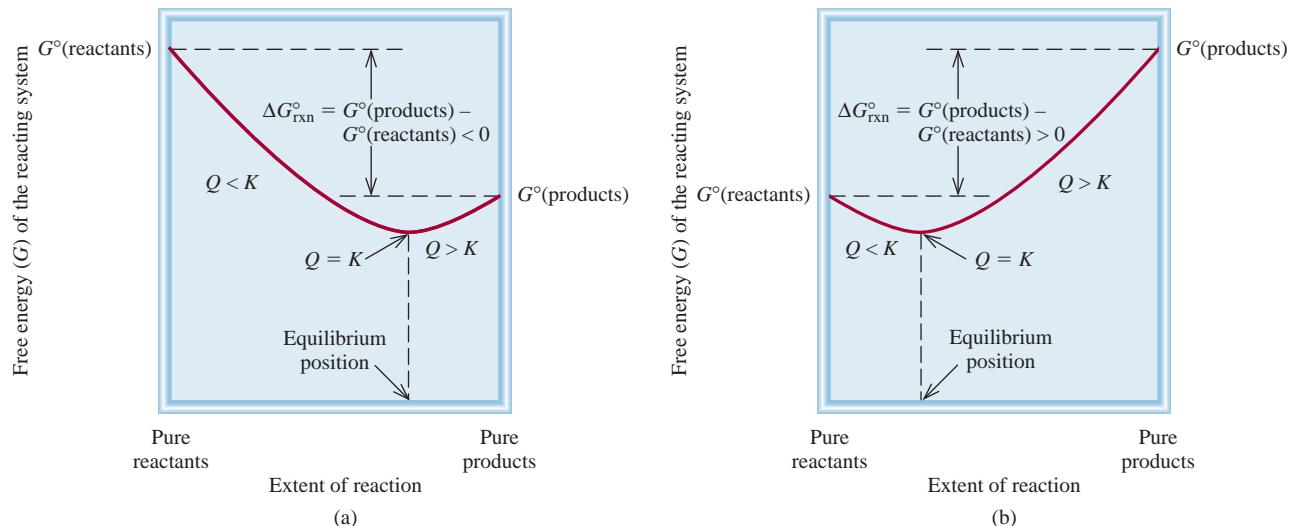
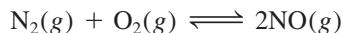


Figure 10.7 (a) $\Delta G_{\text{rxn}}^{\circ} < 0$. At equilibrium, products are favored over reactants. (b) $\Delta G_{\text{rxn}}^{\circ} > 0$. At equilibrium, reactants are favored over products. In both cases, the net reaction toward equilibrium is from left to right (products to reactants) if $Q < K$ and right to left (reactants to products) if $Q > K$. At equilibrium $Q = K$.

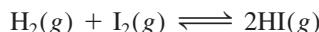
concentrations of all the reacting species. Consider, for example, the formation of nitric oxide from molecular nitrogen and molecular oxygen:



At 25°C, the equilibrium constant K is

$$K = \frac{P_{\text{NO}}^2}{P_{\text{N}_2} P_{\text{O}_2}} = 1.9 \times 10^{-31}$$

The very small value of K means that the concentration of NO at equilibrium will be exceedingly low, making it difficult to measure. In such a case, the equilibrium constant is more conveniently obtained from $\Delta G_{\text{rxn}}^\circ$. [As discussed in Section 8.6, $\Delta G_{\text{rxn}}^\circ$ can be calculated from $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$ or determined directly from Gibbs free energy of formation (ΔG_f°) data.] On the other hand, the equilibrium constant for the formation of hydrogen iodide from molecular hydrogen and molecular iodine is near unity at room temperature:

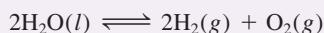


For this reaction, it is easier to measure K and then calculate $\Delta G_{\text{rxn}}^\circ$ using Equation 10.12 than to measure $\Delta H_{\text{rxn}}^\circ$ and $\Delta S_{\text{rxn}}^\circ$ and use Equation 8.35.

Examples 10.8 to 10.10 show how to use Equations 10.11 and 10.12 to calculate K and $\Delta G_{\text{rxn}}^\circ$.

Example 10.8

Using data listed in Appendix 2, calculate the equilibrium constant K for the following reaction at 25°C:



Strategy According to Equation 10.12, the equilibrium constant for the reaction is related to the standard free energy change: $\Delta G_{\text{rxn}}^\circ = -RT \ln K$. Therefore, we first need to calculate $\Delta G_{\text{rxn}}^\circ$ by following the procedure in Example 8.9. Using that value, we can then calculate K . Remember to use appropriate units for T .

Solution According to Equation 8.34,

$$\begin{aligned}\Delta G_{\text{rxn}}^\circ &= [2\Delta G_f^\circ(\text{H}_2) + \Delta G_f^\circ(\text{O}_2)] - [2\Delta G_f^\circ(\text{H}_2\text{O})] \\ &= [2(0 \text{ kJ mol}^{-1}) + (0 \text{ kJ mol}^{-1})] - [2(-237.1 \text{ kJ mol}^{-1})] \\ &= +474.2 \text{ kJ mol}^{-1}\end{aligned}$$

Using Equation 10.12,

$$\begin{aligned}\Delta G_{\text{rxn}}^\circ &= -RT \ln K \\ \ln K &= -\frac{\Delta G_{\text{rxn}}^\circ}{RT} \\ \ln K &= -\frac{474.2 \text{ kJ mol}^{-1}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = -191.3 \\ K &= e^{-191.3} = 8.3 \times 10^{-84}\end{aligned}$$

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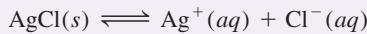
Comment This extremely small equilibrium constant is consistent with the fact that water does not decompose into hydrogen and oxygen gases at 25°C. Thus, a large positive $\Delta G_{\text{rxn}}^{\circ}$ favors reactants over products at equilibrium.

Practice Exercise Calculate the equilibrium constant K at 25°C for the reaction



Example 10.9

If solid AgCl is placed into water, some amount will dissolve according to the equilibrium



The equilibrium constant for this dissolution reaction (called the *solubility product*, K_{sp}) is 1.6×10^{-10} at 25°C. Calculate $\Delta G_{\text{rxn}}^{\circ}$.

Strategy According to Equation 10.12, the equilibrium constant for the reaction is related to the standard Gibbs free energy change: $\Delta G_{\text{rxn}}^{\circ} = -RT \ln K$.

Solution The solubility equilibrium for AgCl is

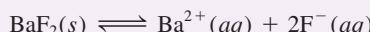
$$\begin{aligned} \text{AgCl}(s) &\rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq) \\ K = K_{\text{sp}} &= \frac{a_{\text{Ag}^+} a_{\text{Cl}^-}}{a_{\text{AgCl}(s)}} \approx \frac{[\text{Ag}^+][\text{Cl}^-]}{1} = [\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10} \end{aligned}$$

Using Equation 10.12 we obtain

$$\begin{aligned} \Delta G_{\text{rxn}}^{\circ} &= -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K}) \ln(1.6 \times 10^{-10}) \\ &= 5.6 \times 10^4 \text{ J mol}^{-1} = 56 \text{ kJ mol}^{-1} \end{aligned}$$

Comment Solubility products for ionic compounds are discussed in more detail in Chapter 11.

Practice Exercise Calculate $\Delta G_{\text{rxn}}^{\circ}$ for the following process at 25°C:



The K_{sp} of BaF₂ is 1.7×10^{-6} .

Example 10.10

The equilibrium constant K for the reaction



is 0.115 at 298 K, which corresponds to a standard free-energy change of 5.36 kJ mol⁻¹. In a certain experiment, the initial pressures are $P_{\text{NO}_2} = 0.124$ bar and $P_{\text{N}_2\text{O}_4} = 0.459$ bar. Calculate ΔG_{rxn} for the reaction at these pressures, and predict the direction of the net reaction.

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Strategy According to the information given in the problem statement, neither the reactant nor the product is at its standard state of 1 bar. To determine the direction of the net reaction, we need to calculate the free-energy change under nonstandard-state conditions (ΔG_{rxn}) using Equation 10.11 and the given $\Delta G_{\text{rxn}}^{\circ}$ value. The partial pressures are expressed as dimensionless quantities in the reaction quotient Q .

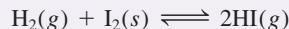
Solution Equation 10.11 can be written as

$$\begin{aligned}\Delta G_{\text{rxn}} &= \Delta G_{\text{rxn}}^{\circ} + RT \ln Q \\ &= \Delta G_{\text{rxn}}^{\circ} + RT \ln \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} \\ &= 5.40 \times 10^3 \text{ J mol}^{-1} + (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \ln \frac{(0.123)^2}{0.459} \\ &= 5.40 \times 10^3 \text{ J mol}^{-1} - 8.46 \times 10^3 \text{ J mol}^{-1} \\ &= -3.06 \times 10^3 \text{ J mol}^{-1} = -3.06 \text{ kJ mol}^{-1}\end{aligned}$$

Because $\Delta G_{\text{rxn}} < 0$, the net reaction proceeds from left to right to reach equilibrium.

Check Although $\Delta G_{\text{rxn}}^{\circ} > 0$, the reaction can be made to favor product formation initially by having a small concentration (pressure) of the product compared to that of the reactant. Confirm this prediction by showing that $Q < K$.

Practice Exercise The $\Delta G_{\text{rxn}}^{\circ}$ for the reaction

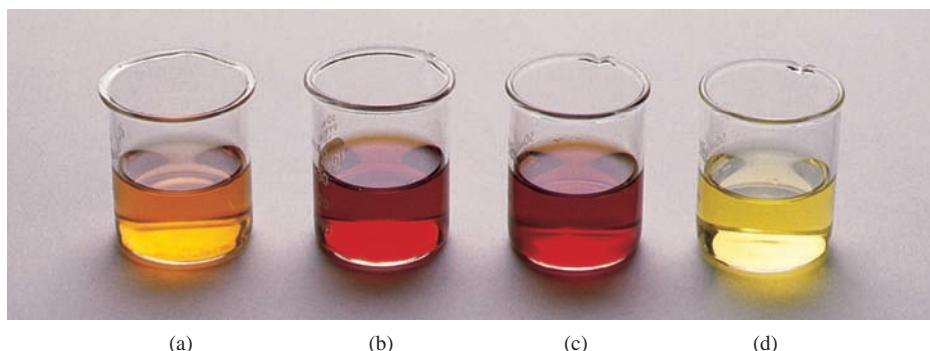


is 3.40 kJ mol⁻¹ at 25°C. In one experiment, the initial pressures are $P_{\text{H}_2} = 0.426$ bar, $P_{\text{I}_2} = 0.240$ bar, and $P_{\text{HI}} = 0.235$ bar. Calculate ΔG_{rxn} for the reaction, and predict the direction of the net reaction.

10.4 | The Response of an Equilibrium System to a Change in Conditions Can Be Determined Using Le Châtelier's Principle

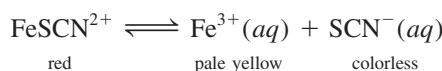
There is a general rule that helps us to predict the direction in which an equilibrium reaction will move when a change in concentration, pressure, volume, or temperature occurs. The rule, known as *Le Châtelier's³ principle*, states that *if an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position*. The word *stress* here means a change in concentration, pressure, volume, or temperature that removes the system from the equilibrium state. We will use Le Châtelier's principle to assess the effects of such changes.

3. Henri Louis Le Châtelier (1850–1936). French chemist. Le Châtelier contributed to our understanding of metallurgy, cements, glasses, fuels, and explosives. He was also noted for his skills in industrial management.



Changes in Concentration

Iron(III) thiocyanate $[\text{Fe}(\text{SCN})_3]$ dissolves readily in water to give an equilibrium mixture of undissociated FeSCN^{2+} and Fe^{3+} and SCN^- ions:



The solution appears orange [Figure 10.8(a)] because hydrated FeSCN^{2+} ions are red and $\text{Fe}^{3+}(aq)$ ions are pale yellow. What happens if we add some sodium thiocyanate (NaSCN) to this solution? In this case, the stress applied to the equilibrium system is an increase in the concentration of SCN^- (from the dissociation of NaSCN). To offset this stress, some Fe^{3+} ions react with the added SCN^- ions, and the equilibrium shifts from right to left:



Consequently, the red color of the solution deepens [Figure 10.8(b)]. Similarly, if we added iron(III) nitrate $[\text{Fe}(\text{NO}_3)_3]$ to the original solution, the red color would also deepen [Figure 10.8(c)] because the additional Fe^{3+} ions [from $\text{Fe}(\text{NO}_3)_3$] would shift the equilibrium from right to left.

Now suppose we add some oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) to the original solution. Oxalic acid ionizes in water to form the oxalate ion ($\text{C}_2\text{O}_4^{2-}$), which binds strongly to the Fe^{3+} ions:



The formation of the stable yellow ion $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ removes free Fe^{3+} ions in solution. Consequently, more FeSCN^{2+} units dissociate and the equilibrium shifts from left to right:

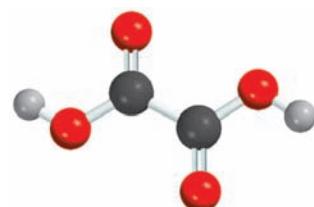


The red solution will turn yellow due to the formation of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ ions along with the production of more Fe^{3+} ions [Figure 10.8(d)].

This experiment demonstrates that all reactants and products are present in the reacting system at equilibrium. Additionally, increasing the concentrations of the products (Fe^{3+} or SCN^-) shifts the equilibrium to the left, whereas decreasing the concentration of the product Fe^{3+} shifts the equilibrium to the right. These results are just as predicted by Le Châtelier's principle.

The effect of a change in concentration on the equilibrium position is shown in Example 10.11.

Figure 10.8 Effect of concentration change on the position of equilibrium. (a) An aqueous $\text{Fe}(\text{SCN})_3$ solution. The color of the solution is due to both the red FeSCN^{2+} and the yellow Fe^{3+} species. (b) After the addition of some NaSCN to the solution in (a), the equilibrium shifts to the left. (c) After the addition of some $\text{Fe}(\text{NO}_3)_3$ to the solution in (a), the equilibrium shifts to the left as well. (d) After the addition of some $\text{H}_2\text{C}_2\text{O}_4$ to the solution in (a), the equilibrium shifts to the right. The yellow color is due to the presence of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ ions.

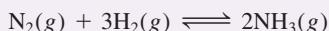


Oxalic acid is sometimes used to remove bathtub rings that consist of rust, or Fe_2O_3 .

Le Châtelier's principle simply summarizes the observed behavior of equilibrium systems; therefore, it is incorrect to say that a given equilibrium shift occurs "because of" Le Châtelier's principle.

Example 10.11

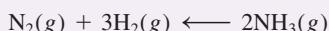
At 720°C, the equilibrium constant K_c for the reaction



is 2.37×10^{-3} . In a certain experiment, the equilibrium concentrations are $[\text{N}_2] = 0.683 M$, $[\text{H}_2] = 8.80 M$, and $[\text{NH}_3] = 1.05 M$. Suppose some NH_3 is added to the mixture so that its concentration is increased to $3.65 M$. (a) Use Le Châtelier's principle to predict the shift in direction of the net reaction to reach a new equilibrium. (b) Confirm your prediction by calculating the reaction quotient Q_c and comparing its value with K_c .

Strategy (a) Determine the stress that is applied to the system, and then apply Le Châtelier's principle to determine the direction in which the equilibrium will respond. (b) At the instant when some NH_3 is added, the system is no longer at equilibrium. Calculate Q_c for the reaction at this point, and compare its value to K_c to determine the direction of the net reaction to reach equilibrium.

Solution (a) The stress applied to the system is the addition of NH_3 (the reaction product). To offset this stress, some NH_3 must react to produce N_2 and H_2 (the reactants) until a new equilibrium is established. The net reaction therefore shifts from right to left:



(b) The reaction quotient is given by

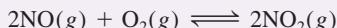
$$Q_c = \frac{[\text{NH}_3]^2}{[\text{N}_2]_0[\text{H}_2]^3} = \frac{(3.65)^2}{(0.683)(8.80)^3} = 2.86 \times 10^{-2}$$

Because this value is greater than 2.37×10^{-3} (the value of K_c), the net reaction shifts from right to left (towards reactants) until Q_c equals K_c .

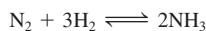
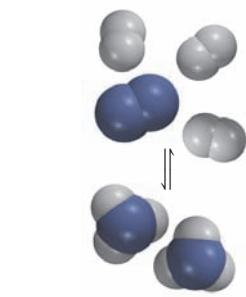
Figure 10.9 shows qualitatively the changes in concentrations of the reacting species.

Check Both the analysis using Le Châtelier's principle and the analysis comparing the values of Q_c and K_c give the same result: the reaction proceeds from left to right until equilibrium is reestablished.

Practice Exercise At 430°C, the equilibrium constant (K_p) for the reaction



is 1.5×10^5 . In one experiment, the initial pressures of NO , O_2 , and NO_2 at equilibrium are 1.1×10^{-2} , 1.1×10^{-3} , and 0.14 bar, respectively. Suppose enough O_2 is added to the system to increase the partial pressure of O_2 to 5.3×10^{-3} bar. (a) Use Le Châtelier's principle to predict which way the reaction will shift to restore equilibrium. (b) Confirm your answer in part (a) by calculating Q_p and comparing it to K_p .



Initial equilibrium Change Final equilibrium

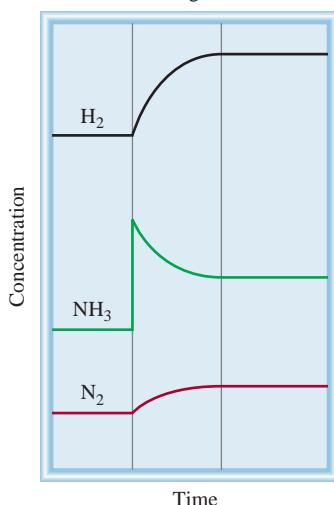


Figure 10.9 Changes in the concentrations of H_2 , N_2 , and NH_3 after the addition of NH_3 to the equilibrium mixture. The changes are consistent with Le Châtelier's principle.

Response of Equilibrium to Changes in Pressure

Changes in pressure ordinarily do not affect the concentrations of reacting species in condensed phases (e.g., in an aqueous solution) because liquids and solids are virtually incompressible. Concentrations of gases, on the other hand, are greatly affected by changes in pressure. Suppose, for example, that the equilibrium system



is in a cylinder fitted with a movable piston. What happens if we increase the pressure on the gases by pushing down on the piston at constant temperature? The equilibrium constant expression for this system (assuming ideal gas behavior) is

$$K_P = \frac{(P_{\text{NO}_2}/P_0)^2}{P_{\text{N}_2\text{O}_4}/P_0}$$

This expression contains only the partial pressures, not the total pressure. Using Dalton's law of partial pressures ($P_i = x_i P$) gives

$$\begin{aligned} K_P &= \frac{(x_{\text{NO}_2} P/P_0)^2}{x_{\text{N}_2\text{O}_4} P/P_0} = \frac{x_{\text{NO}_2}^2}{x_{\text{N}_2\text{O}_4}} \left(\frac{P}{P_0} \right) \\ K_P &= K_x \frac{P}{P_0} \end{aligned} \quad (10.13)$$

where we have introduced a new kind of equilibrium constant, K_x , which is the equilibrium constant in terms of mole fractions. For a general ideal gas reaction, Equation 10.13 becomes

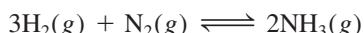
$$K_P = K_x \left(\frac{P}{P_0} \right)^{\Delta n} \quad (10.14)$$

where Δn is as previously defined in Equation 10.6:

$$\Delta n = \text{moles of gaseous products} - \text{moles of gaseous reactants}$$

For a given temperature, K_P is a constant, independent of total pressure. From Equation 10.14, therefore, the changes in concentration due to a change in the pressure (as measured by K_x) will depend upon the value of Δn for the specific reaction. We can identify the following three cases:

- ▶ **$\Delta n > 0$:** The reaction as written results in a net *increase* in the total number of molecules in going from reactant to product. For this case, increasing the pressure increases the term $(P/P_0)^{\Delta n}$, so for K_P to remain constant, K_x must decrease, resulting in the reaction shifting toward the reactants. (A smaller K_x means that the mole fractions of the products decrease and those of the reactants increase.) The reaction $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ falls into this category (Figure 10.10).
- ▶ **$\Delta n < 0$:** The reaction as written results in a net *decrease* in the total number of molecules in going from reactant to product. For this case, increasing the pressure decreases the term $(P/P_0)^{\Delta n}$, so for K_P to remain constant, K_x must increase, resulting in the reaction shifting toward the products. (A larger K_x means that the mole fractions of the reactants decrease and those of the products increase.) An example of this type of reaction is



- ▶ **$\Delta n = 0$:** The reaction as written results in no net change in the total number of molecules present as the reaction proceeds from left to right. For this case, $K_P = K_x$ and changing the pressure has no effect on the relative amount of reactants and products. An example of this type of reaction is

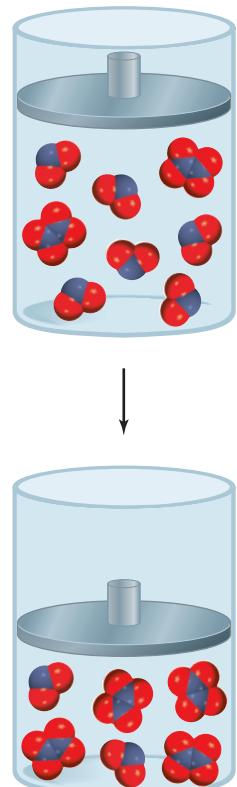
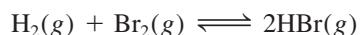


Figure 10.10 Qualitative illustration showing the effect of an increase in pressure on the $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ equilibrium. The reaction shifts toward the reactants in order to reestablish equilibrium.

The response of a gas-phase equilibrium to pressure changes is an example of Le Châtelier's principle, where the stress is the change in pressure. When the pressure of a reaction mixture at equilibrium is increased, the system will respond by shifting the equilibrium in a direction that decreases the pressure, that is, in the direction that reduces the number of gas-phase molecules in the reaction mixture.

It is possible to change the pressure of a system without changing its volume. Suppose the $\text{NO}_2\text{-N}_2\text{O}_4$ system is contained in a stainless-steel vessel whose volume is constant. We can increase the total pressure in the vessel by adding an inert gas (e.g., helium) to the equilibrium system. Adding helium to the equilibrium mixture at constant volume increases the total gas pressure and decreases the mole fractions of both NO_2 and N_2O_4 , but the partial pressure of each gas, given by the product of its mole fraction and total pressure, does not change. Thus, the presence of the inert gas does not affect the equilibrium.

Examples 10.12 and 10.13 show how pressure changes affect the equilibrium position.

Example 10.12

Consider the following equilibrium systems:

- $2\text{PbS}(s) + 3\text{O}_2(g) \rightleftharpoons 2\text{PbO}(s) + 2\text{SO}_2(g)$
- $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$
- $\text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) + \text{CO}(g)$

In each case, predict the direction of the net reaction when the pressure of the system is increased (the volume is decreased) at constant temperature.

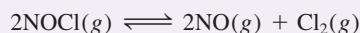
Strategy A change in pressure can affect the volume of a gas, but not the volume of a solid or liquid because solids and liquids are far less compressible than gases. The stress applied is an increase in pressure. According to Le Châtelier's principle, the system will adjust to partially offset this stress. In other words, the system will adjust to decrease the pressure. This can be achieved by shifting the equilibrium to the side of the equation that has fewer moles of gas.

Solution (a) Consider only the gaseous molecules. In the balanced equation, there are 3 moles of gaseous reactants and 2 moles of gaseous products. Therefore, $\Delta n = 2 - 3 = -1$ and the net reaction will shift toward the products (to the right) when the pressure is increased.

- The number of moles of products is 2 and that of reactants is 1; therefore, $\Delta n = 2 - 1 = +1$ and the net reaction will shift to the left, toward the reactant.
- The number of moles of products is equal to the number of moles of reactants ($\Delta n = 0$), so a change in pressure will have very little effect (if any) on the equilibrium.⁴

Check In each case, the prediction is consistent with Le Châtelier's principle.

Practice Exercise Consider the following equilibrium reaction involving nitrosyl chloride, nitric oxide, and molecular chlorine:

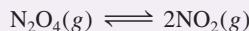


Predict the direction of the net reaction when the pressure of the system is decreased (the volume is increased) at constant temperature.

4. Equation 10.14 assumes that all gases behave ideally. For real gases, some pressure dependence on the gas-phase equilibrium, due to nonideality, is possible if $\Delta n = 0$, but such effects are usually very small.

Example 10.13

Consider a gas-phase reaction vessel in which only NO_2 and N_2O_4 are present. These species undergo the reversible reaction



The equilibrium constant K_P for this reaction is 0.115 at 298 K. Calculate the mole fractions of NO_2 and N_2O_4 if the total pressure is (a) 1.00 bar and (b) 5.00 bar. Are your conclusions consistent with Le Châtelier's principle? (For this particular reaction, it is unnecessary to know the initial amounts of each species.)

Strategy The mole fractions can be obtained if we know K_x . The relationship between K_P and K_x is given in Equation 10.14. Here $\Delta n = 1$.

Solution (a) Equation 10.14 with $\Delta n = 1$ gives

$$K_P = K_x \left(\frac{P}{P_o} \right) \quad \text{or} \quad K_x = K_P \left(\frac{P_o}{P} \right)$$

For $P = 1.00$ bar, $K_x = K_P = 0.115$. For this reaction,

$$K_x = \frac{x_{\text{NO}_2}^2}{x_{\text{N}_2\text{O}_4}} = \frac{x_{\text{NO}_2}^2}{1 - x_{\text{NO}_2}} = 0.115$$

where we have used the relationship $x_{\text{N}_2\text{O}_4} = 1 - x_{\text{NO}_2}$. Multiplying through by the denominator on both sides gives

$$\begin{aligned} x_{\text{NO}_2}^2 &= 0.115(1 - x_{\text{NO}_2}) \\ x_{\text{NO}_2}^2 + 0.115x_{\text{NO}_2} - 0.115 &= 0 \end{aligned}$$

The solutions to this quadratic equation are $x_{\text{NO}_2} = -0.401$ and $+0.286$. Mole fractions must be positive, so the first solution is physically impossible. At $P = 1.00$ bar, therefore,

$$\begin{aligned} x_{\text{NO}_2} &= 0.286 \\ x_{\text{N}_2\text{O}_4} &= 1 - x_{\text{NO}_2} = 0.714 \end{aligned}$$

(b) At $P = 5$ bar, we have

$$K_x = K_P \frac{P_o}{P} = 0.115 \times \frac{1 \text{ bar}}{5.00 \text{ bar}} = 0.0230$$

Proceeding as in (a), the quadratic equation is

$$x_{\text{NO}_2}^2 + 0.0230x_{\text{NO}_2} - 0.0230 = 0$$

The solutions to this quadratic equation are $x_{\text{NO}_2} = -0.164$ and $+0.140$. Mole fractions must be positive, so the second solution is the plausible one. At $P = 5.00$ bar, therefore,

$$\begin{aligned} x_{\text{NO}_2} &= 0.140 \\ x_{\text{N}_2\text{O}_4} &= 1 - x_{\text{NO}_2} = 0.860 \end{aligned}$$

According to Le Châtelier's principle, increasing the pressure from 1 bar to 5 bar will shift the reaction in the direction that contains fewer molecules (in this case, to the left), so the equilibrium mole fraction of N_2O_4 will increase, as is observed.

Check Make sure the mole fractions for the two species add to 1. If the mole fractions and pressures are substituted into Equation 10.14, the correct value of K_P (0.115) should be obtained.

—Continued

Continued—

Practice Exercise The equilibrium constant for the reaction



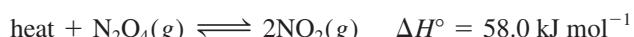
is 0.411 at 500 K. If only pure $\text{PCl}_5(g)$ is present in the container initially, calculate the mole fractions of PCl_5 , PCl_3 , and Cl_2 at equilibrium at a pressure of (a) 1 bar and (b) 7 bar. Are your conclusions consistent with Le Châtelier's principle? (Hint: Think about the stoichiometric relationships between the mole fractions for this system.)

Changes in Temperature

A change in concentration, pressure, or volume may alter the equilibrium position (that is, the relative amounts of reactants and products), but it does not change the value of the equilibrium constant. Only a change in temperature can alter the equilibrium constant. To see why, consider again the following reaction:



The forward reaction is endothermic (absorbs heat, $\Delta H^\circ > 0$)



so the reverse reaction is exothermic (releases heat, $H^\circ < 0$):



At equilibrium at a certain temperature, the heat effect is zero because there is no net reaction. If we treat heat as though it were a chemical reagent, then a rise in temperature “adds” heat to the system and a drop in temperature “removes” heat from the system. As with a change in any other parameter (concentration, pressure, or volume), the system shifts to reduce the effect of the change. Therefore, a temperature increase favors the endothermic direction (from left to right in the equilibrium equation) and a temperature decrease favors the exothermic direction (from right to left in the equilibrium equation). Consequently, the equilibrium constant increases when the system is heated and decreases when the system is cooled (Figure 10.11).

As another example, consider the equilibrium between the following ions:

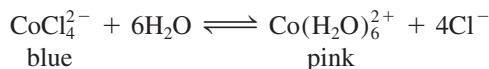
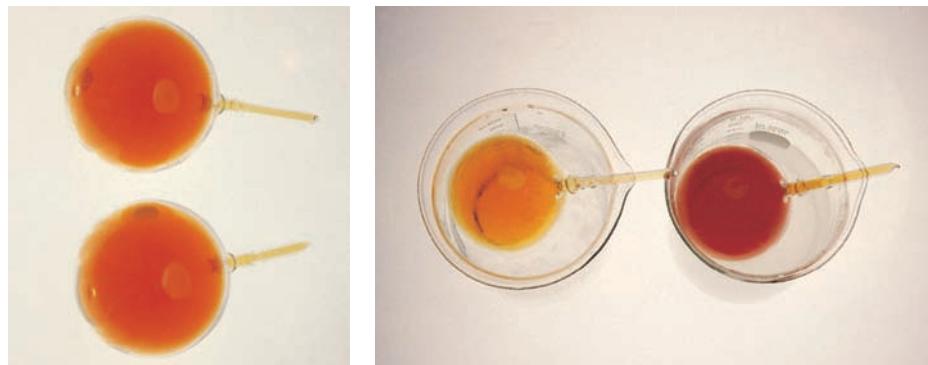


Figure 10.11 (a) Two bulbs containing a mixture of NO_2 and N_2O_4 gases at equilibrium. (b) When one bulb is immersed in ice water (left), its color becomes lighter, indicating the formation of colorless N_2O_4 gas. When the other bulb is immersed in hot water, its color darkens, indicating an increase in NO_2 .



(a)

(b)

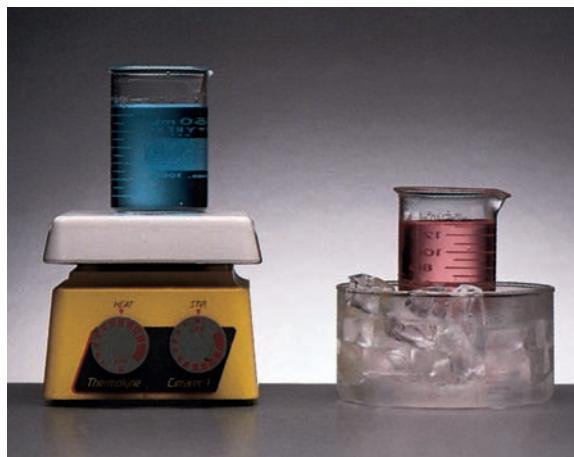


Figure 10.12 (Left) Heating favors the formation of the blue CoCl_4^{2-} ion. (Right) Cooling favors the formation of the pink $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ion.

The formation of CoCl_4^{2-} is endothermic. On heating, the equilibrium shifts to the left and the solution turns blue. Cooling favors the exothermic reaction [the formation of $\text{Co}(\text{H}_2\text{O})_6^{2+}$, and the solution turns pink (Figure 10.12). In summary, *a temperature increase favors an endothermic reaction, and a temperature decrease favors an exothermic reaction*.

We can quantify the change in the equilibrium constant due to changes in temperature using the relationship between $\Delta G_{\text{rxn}}^\circ$ and K (Equation 10.12):

$$\Delta G_{\text{rxn}}^\circ = -RT \ln K$$

or

$$\ln K = -\frac{\Delta G^\circ}{RT}$$

If we subtract the values for $\ln K$ at two different temperature (T_1 and T_2), we get

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = -\left(\frac{\Delta G_{T_2}^\circ}{RT_2} - \frac{\Delta G_{T_1}^\circ}{RT_1}\right)$$

Using the relation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (Equation 8.35), we have

$$\ln \frac{K_2}{K_1} = -\left(\frac{\Delta H_{T_2}^\circ - T_2 \Delta S_{T_2}^\circ}{RT_2} - \frac{\Delta H_{T_1}^\circ - T_1 \Delta S_{T_1}^\circ}{RT_1}\right)$$

Rearranging gives

$$\ln \frac{K_2}{K_1} = \frac{1}{R} \left(\frac{\Delta H_{T_2}^\circ}{T_1} - \frac{\Delta H_{T_1}^\circ}{T_2} + \Delta S_{T_2}^\circ - \Delta S_{T_1}^\circ \right) \quad (10.15)$$

As discussed in Section 8.4, we can often assume, to a good approximation, that ΔH° and ΔS° are independent of temperature as long as the range of temperatures is not too great. Applying this assumption to Equation 10.15 gives

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (10.16)$$

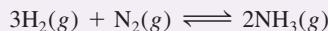
This equation, which relates the equilibrium constant at one temperature to that at another temperature assuming that ΔH° and ΔS° are approximately constant over the temperature range, is called the ***van't Hoff equation***.

Equation 10.16 is a mathematical statement of Le Châtelier's principle for the change in the equilibrium constant with changes in temperature. Suppose that $T_2 > T_1$. If the reaction is endothermic ($\Delta H^\circ > 0$), the right-hand side of the equation will be positive and $K_2 > K_1$, that is, the reaction shifts toward the products in an endothermic reaction, consistent with Le Châtelier's principle. If the reaction is exothermic ($\Delta H^\circ < 0$), the right-hand side of the equation will be negative and $K_2 < K_1$, that is, the reaction shifts toward the reactants in an exothermic reaction.

Example 10.14 shows how to use Equation 10.16 to determine the change in the equilibrium constant with a change in temperature.

Example 10.14

The equilibrium constant for the reaction



is 5.58×10^5 at 25°C . Determine the equilibrium constant for this reaction at 200°C .

Strategy We are given K_1 , T_1 , and T_2 , so we need to know ΔH° for this reaction in order to use Equation 10.16 to determine K_2 . We can determine ΔH° using the data in Appendix 2. Don't forget to convert the temperatures from degrees Celsius to kelvins before using Equation 10.16.

Solution The standard enthalpy change for this reaction (ΔH°) can be found from the standard enthalpies of formation for the reactants and products.

$$\begin{aligned}\Delta H^\circ &= 2\Delta H_f^\circ(\text{NH}_3) - 3\Delta H_f^\circ(\text{H}_2) - \Delta H_f^\circ(\text{N}_2) \\ &= 2(-45.9 \text{ kJ mol}^{-1}) - 3(0) - (0) = -91.8 \text{ kJ mol}^{-1}\end{aligned}$$

For this problem $T_1 = 298.15 \text{ K}$ and $T_2 = 473.15 \text{ K}$. Substitution into Equation 10.16 gives

$$\begin{aligned}\ln \frac{K_2}{K_1} &= \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ &= \frac{-91.8 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{473.15 \text{ K}} \right) \\ &= -13.7\end{aligned}$$

The equilibrium constant K_1 is 5.58×10^5 at 25°C (T_1), so

$$\begin{aligned}\frac{K_2}{K_1} &= e^{-13.7} = 1.12 \times 10^{-6} \\ K_2 &= (1.12 \times 10^{-6})K_1 = (1.12 \times 10^{-6})(5.58 \times 10^5) = 0.625\end{aligned}$$

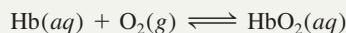
Thus, the equilibrium constant for this reaction decreases with increasing temperature; this is consistent with Le Châtelier's principle for an exothermic reaction.

Practice Exercise The equilibrium constant for the reaction $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ is 0.115 at 298 K. At what temperature would the equilibrium constant be equal to 1?

Life at High Altitudes and Hemoglobin Production

In the human body, countless chemical equilibria must be maintained to ensure physiological well-being. If environmental conditions change, the body must adapt to keep functioning. The consequences of a sudden change in altitude dramatize this fact. Flying from San Francisco, which is at sea level, to Mexico City, where the elevation is 2.3 km (1.4 mi), or scaling a 3-km mountain in two days can cause headache, nausea, extreme fatigue, and other discomforts. These conditions are all symptoms of hypoxia, a deficiency in the amount of oxygen reaching body tissues. In serious cases, the victim may slip into a coma and die if not treated quickly enough. A person living at a high altitude for weeks or months, however, gradually recovers from altitude sickness and adjusts to the low oxygen content in the atmosphere, so that he or she can function normally.

The combination of oxygen with the hemoglobin (Hb) molecule, which carries oxygen through the blood, is a complex reaction, but for our purposes it can be represented by the following simplified equation:



where HbO_2 is oxyhemoglobin, the hemoglobin-oxygen complex that actually transports oxygen to tissues. The equilibrium constant for this reaction is

$$K = \frac{[\text{HbO}_2]}{[\text{Hb}] P_{\text{O}_2}}$$

At an altitude of 3 km, the partial pressure of oxygen is only about 0.14 bar, compared with 0.20 bar at sea level. According

to Le Châtelier's principle, a decrease in the oxygen partial pressure will shift the hemoglobin-oxyhemoglobin equilibrium from right to left. This change depletes the supply of oxyhemoglobin, causing hypoxia. Given enough time, the body copes with this condition by producing more hemoglobin molecules. The equilibrium will then gradually shift back toward the formation of oxyhemoglobin. It takes two to three weeks for the increase in hemoglobin production to meet the body's basic needs adequately. Studies show that long-time residents of high altitude areas have high hemoglobin levels in their blood—sometimes as much as 50% more than individuals living at sea level!



Mountaineers need weeks or even months to become acclimatized to the reduced level of oxygen in the air before scaling summits such as Mount Everest.

Summary of Facts and Concepts

Section 10.1

- ▶ Chemical equilibrium is a dynamic process in which there is no *net* change in the concentrations of reactants and products.
- ▶ For the general chemical reaction



the activities of reactants and products at equilibrium are related by the equilibrium constant expression (Equation 10.2).

- ▶ In many important cases, the activity of a species can be approximated by a simple expression

—*Gases at low to moderate pressure:* $a_i \approx P_i/P^\circ$ (Equation 10.3), where P_i is the partial pressure of the gas and P° is the standard pressure (1 bar).

—*Dilute solutes:* $a_i \approx [i]/c^\circ$ (Equation 10.4), where $[i]$ is the concentration of species i and c° is the standard concentration (1 mol L^{-1}).

—*Pure solids and liquids:* $a_i = 1$.

- ▶ A chemical equilibrium process in which all reactants and products are in the same phase is homogeneous. If the reactants and products are not all in the same phase, the equilibrium is heterogeneous.
- ▶ If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.
- ▶ The value of K depends on how the chemical equation is balanced, and the equilibrium constant for the reverse of a particular reaction is the reciprocal of the equilibrium constant of that reaction.

- The equilibrium constant is the ratio of the rate constant for the forward reaction to that for the reverse reaction.

Section 10.2

- The reaction quotient Q has the same form as the equilibrium constant, but it applies to a reaction that may not be at equilibrium. If $Q > K$, the reaction will proceed from right to left to achieve equilibrium. If $Q < K$, the reaction will proceed from left to right to achieve equilibrium.
- The equilibrium constant can be used to determine the equilibrium concentrations (or pressures) if the initial concentrations (or pressures) are known.

Section 10.3

- The form of the equilibrium constant is a consequence of the Gibbs free energy of mixing

- The equilibrium constant of a reaction and the standard Gibbs free energy change are related by the equation $\Delta G^\circ = -RT \ln K$ (Equation 10.12).

Section 10.4

- Le Châtelier's principle states that if an external stress is applied to a system at chemical equilibrium, the system will adjust to partially offset the stress.
- Only a change in temperature changes the value of the equilibrium constant for a particular reaction. Changes in concentration, pressure, or volume may change the equilibrium concentrations of reactants and products.
- The change in the equilibrium constant with temperature is determined by the standard enthalpy change for a reaction using the van't Hoff equation (Equation 10.16).

Key words

activity, p. 514

chemical equilibrium, p. 512

concentration equilibrium

constant, p. 518

equilibrium

constant, p. 513

heterogeneous

equilibrium, p. 519

homogeneous

equilibrium, p. 516

law of mass action, p. 513

Le Châtelier's principle, p. 536

reaction quotient, p. 525

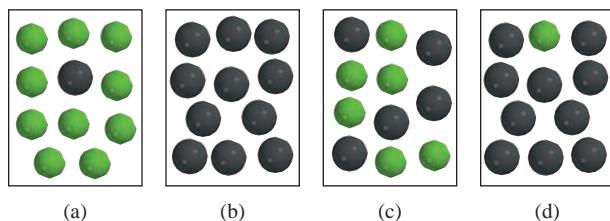
reversible reactions, p. 512

van't Hoff equation, p. 544

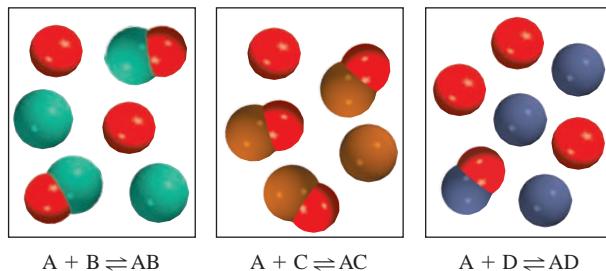
Problems

The Equilibrium Constant Governs the Concentration of Reactants and Products at Equilibrium

- 10.1 The equilibrium constant for the reaction $A \rightleftharpoons B$ is $K_c = 10$ at a certain temperature. (a) Starting with only reactant A, which of the following diagrams best represents the system at equilibrium? (b) Which of the diagrams best represents the system at equilibrium if $K_c = 0.10$? Explain why you can calculate K_c in each case without knowing the volume of the container. The gray spheres represent the A molecules and the green spheres represent the B molecules.



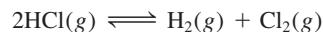
- 10.2 The following diagrams represent the equilibrium state for three different reactions of the type $A + X \rightleftharpoons AX$ ($X = B, C$, or D):



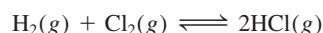
- (a) Which reaction has the largest equilibrium constant?

- (b) Which reaction has the smallest equilibrium constant?

- 10.3 The equilibrium constant K_c for the reaction

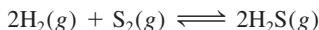


is 4.17×10^{-34} at 25°C . What is the equilibrium constant for the reaction



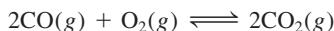
at the same temperature?

- 10.4 Consider the following equilibrium process at 700°C:



Analysis shows that there are 2.50 moles of H₂, 1.35 × 10⁻⁵ mole of S₂, and 8.70 moles of H₂S present in a 12.0-L flask. Calculate the equilibrium constants K_P and K_c for the reaction.

- 10.5 What is K_P at 1273°C for the reaction



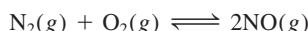
if K_c is 2.24 × 10⁻²² at the same temperature?

- 10.6 The equilibrium constant K_P for the reaction



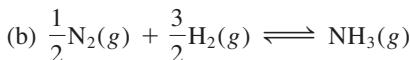
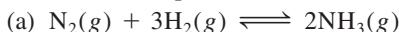
is 1.8 × 10⁻⁵ at 350°C. What is K_c for this reaction?

- 10.7 Consider the following reaction:



If the equilibrium partial pressures of N₂, O₂, and NO at 2200°C are 0.15, 0.33, and 0.051 bar, respectively, what is K_P?

- 10.8 A reaction vessel contains NH₃, N₂, and H₂ at equilibrium at a certain temperature. The equilibrium concentrations are [NH₃] = 0.25 M, [N₂] = 0.11 M, and [H₂] = 1.91 M. Calculate the equilibrium constants K_c and K_P for the synthesis of ammonia if the reaction is represented as



- 10.9 The equilibrium constant K_c for the reaction I₂(g) \rightleftharpoons 2I(g) is 3.8 × 10⁻⁵ at 727°C. Calculate K_c and K_P for the equilibrium 2I(g) \rightleftharpoons I₂(g) at the same temperature.

- 10.10 At equilibrium, the pressure of the reacting mixture



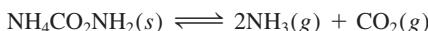
is 0.106 bar at 350°C. Calculate K_P and K_c for this reaction.

- 10.11 The equilibrium constant K_P for the reaction



is 1.05 at 250°C. The reaction starts with a mixture of PCl₅, PCl₃, and Cl₂ at pressures of 0.17, 0.226, and 0.112 bar, respectively, at 250°C. When the mixture comes to equilibrium at that temperature, which pressures will have decreased and which will have increased? Explain why.

- 10.12 Ammonium carbamate (NH₄CO₂NH₂) decomposes as follows:



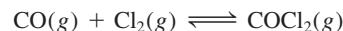
Starting with only the solid, it is found that at 40°C the total gas pressure (NH₃ and CO₂) is 0.367 bar. Calculate the equilibrium constant K_P.

- 10.13 Consider the following reaction at 1600°C:

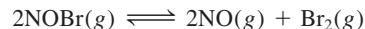


When 1.05 moles of Br₂ are put in a 0.980-L flask, 1.20 percent of the Br₂ undergoes dissociation. Calculate the equilibrium constants K_P and K_c for the reaction.

- 10.14 Pure phosgene gas (COCl₂), 3.00 × 10⁻² mol, was placed in a 1.50-L container. It was heated to 800 K, and at equilibrium the pressure of CO was found to be 0.503 bar. Calculate the equilibrium constant K_P for the reaction

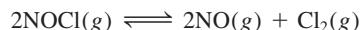


- 10.15 Consider the equilibrium



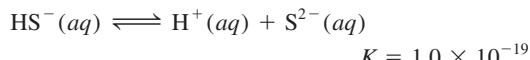
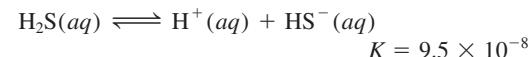
If nitrosyl bromide (NOBr) is 34 percent dissociated at 25°C and the total pressure is 0.25 bar, calculate K_P and K_c for the dissociation at this temperature.

- 10.16 A 2.50-mole quantity of NOCl was initially in a 1.50-L reaction chamber at 400°C. After equilibrium was established, it was found that 28.0 percent of the NOCl had dissociated:



Calculate the equilibrium constant K_P for the reaction.

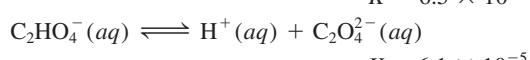
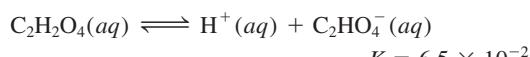
- 10.17 The following equilibrium constants have been determined for hydrosulfuric acid at 25°C:



Calculate the equilibrium constant for the following reaction at the same temperature:



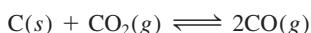
- 10.18 The following equilibrium constants have been determined for oxalic acid at 25°C:



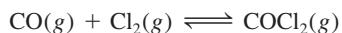
Calculate the equilibrium constant for the following reaction at the same temperature:



- 10.19 The following equilibrium constants were determined at 1123 K:



$$K_P = 1.3 \times 10^{14}$$



$$K_P = 6.0 \times 10^{-3}$$

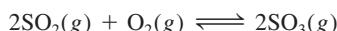
Write the equilibrium constant expression K_P , and calculate the equilibrium constant at 1123 K for



- 10.20 At a certain temperature, the following reactions have the constants shown:

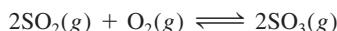


Calculate the equilibrium constant K_c for the following reaction at that temperature:



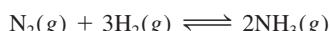
The Equilibrium Constant Can Be Used to Predict the Direction and Equilibrium Concentrations of a Chemical Reaction

- 10.21 The equilibrium constant K_P for the reaction



is 5.53×10^4 at 350°C. The initial pressures of SO_2 and O_2 in a mixture are 0.354 and 0.772 bar, respectively, at 350°C. When the mixture equilibrates, is the total pressure less than or greater than the sum of the initial pressures (1.127 bar)?

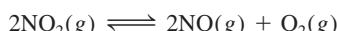
- 10.22 For the synthesis of ammonia



the equilibrium constant K_c at 375°C is 1.2. Starting with $[\text{H}_2]_0 = 0.76 \text{ M}$, $[\text{N}_2]_0 = 0.60 \text{ M}$, and $[\text{NH}_3]_0 = 0.48 \text{ M}$, which gases will have increased in concentration and which will have decreased in concentration when the mixture comes to equilibrium?

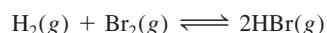
- 10.23 For the reaction $\text{H}_2(g) + \text{CO}_2(g) \rightleftharpoons \text{H}_2\text{O}(g) + \text{CO}(g)$ at 700°C, $K_c = 0.534$. Calculate the number of moles of H_2 that are present at equilibrium if a mixture of 0.300 mole each of CO and H_2O is heated to 700°C in a 10.0-L container.

- 10.24 At 1000 K, a sample of pure NO_2 gas decomposes:



The equilibrium constant K_P is 160. Analysis shows that the partial pressure of O_2 is 0.25 bar at equilibrium. Calculate the pressure of NO and NO_2 in the mixture.

- 10.25 The equilibrium constant K_c for the reaction



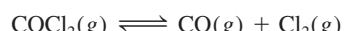
is 2.18×10^6 at 730°C. Starting with 3.20 moles of HBr in a 12.0-L reaction vessel, calculate the concentrations of H_2 , Br_2 , and HBr at equilibrium.

- 10.26 The dissociation of molecular iodine into iodine atoms is represented as



At 1000 K, the equilibrium constant K_c for the reaction is 3.80×10^{-5} . Suppose you start with 0.0456 mole of I_2 in a 2.30-L flask at 1000 K. What are the concentrations of the gases at equilibrium?

- 10.27 The equilibrium constant K_c for the decomposition of phosgene (COCl_2) is 4.69×10^{-3} at 527°C:



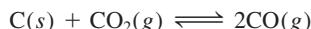
Calculate the equilibrium partial pressure of all the components, starting with pure phosgene at 0.785 bar.

- 10.28 Consider the following equilibrium process at 686°C:



The equilibrium concentrations of the reacting species are $[\text{CO}] = 0.050 \text{ M}$, $[\text{H}_2] = 0.045 \text{ M}$, $[\text{CO}_2] = 0.086 \text{ M}$, and $[\text{H}_2\text{O}] = 0.040 \text{ M}$. (a) Calculate K_c for the reaction at 686°C. (b) If we add CO_2 to increase its concentration to 0.50 mol L^{-1} , what will the concentrations of all the gases be when equilibrium is reestablished?

- 10.29 Consider the heterogeneous equilibrium process:



At 700°C, the total pressure of the system is found to be 4.56 bar. If the equilibrium constant K_P is 1.54, calculate the equilibrium partial pressures of CO_2 and CO .

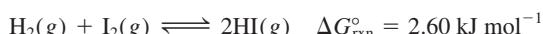
- 10.30 The equilibrium constant K_c for the reaction



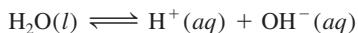
is 4.2 at 1650°C. Initially 0.80 mol H_2 and 0.80 mol CO_2 are injected into a 5.0-L flask. Calculate the concentration of each species at equilibrium.

Thermodynamics and the Equilibrium Constant

- 10.31 Calculate K_P for the following reaction at 25°C:

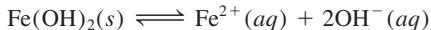


- 10.32 For the autoionization of water at 25°C,



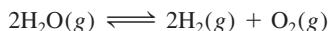
K is 1.0×10^{-14} . What is $\Delta G_{\text{rxn}}^\circ$ for the process?

- 10.33 For the following reaction at 25°C:



K is 1.6×10^{-14} . Calculate $\Delta G_{\text{rxn}}^\circ$ for the reaction.

- 10.34 Using data from Appendix 2, calculate $\Delta G_{\text{rxn}}^\circ$ and K for the following equilibrium reaction at 25°C.



- 10.35 (a) Using the data from Appendix 2, calculate $\Delta G_{\text{rxn}}^\circ$ and K for the following equilibrium reaction at 25°C.



(b) Calculate ΔG_{rxn} for this reaction if the partial pressures of the initial mixture are $P_{\text{PCl}_5} = 0.0029$ bar, $P_{\text{PCl}_3} = 0.27$ bar, and $P_{\text{Cl}_2} = 0.40$ bar.

- 10.36 The equilibrium constant K for the reaction



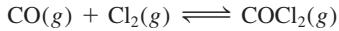
is 4.40 at 2000 K. (a) Calculate $\Delta G_{\text{rxn}}^\circ$ for the reaction. (b) Calculate ΔG_{rxn} for the reaction when the partial pressures are $P_{\text{H}_2} = 0.25$ bar, $P_{\text{CO}_2} = 0.78$ bar, $P_{\text{H}_2\text{O}} = 0.67$ bar, and $P_{\text{CO}} = 1.21$ bar.

- 10.37 Consider the decomposition of calcium carbonate:



Calculate the pressure in bar of CO_2 in an equilibrium process (a) at 25°C and (b) at 800°C. Assume that $\Delta H_{\text{rxn}}^\circ = 177.8 \text{ kJ mol}^{-1}$ and $\Delta S_{\text{rxn}}^\circ = 160.5 \text{ J mol}^{-1} \text{ K}^{-1}$ for the temperature range.

- 10.38 The equilibrium constant K for the reaction



is 5.62×10^{35} at 25°C. Calculate ΔG_f° for COCl_2 at 25°C.

- 10.39 Using the data from Appendix 2, calculate $\Delta G_{\text{rxn}}^\circ$ for the process



Is the formation of graphite from diamond favored at 25°C? If so, why is it that diamonds do not become graphite on standing?

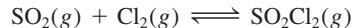
- 10.40 At 25°C, $\Delta G_{\text{rxn}}^\circ$ for the process



is 8.6 kJ mol^{-1} . Calculate the vapor pressure of water at this temperature.

The Response of an Equilibrium System to a Change in Conditions Can Be Determined Using Le Châtelier's Principle

- 10.41 Consider the following equilibrium system involving SO_2 , Cl_2 , and SO_2Cl_2 (sulfuryl dichloride):



Predict how the equilibrium position would change if (a) Cl_2 gas were added to the system; (b) SO_2Cl_2 were removed from the system; or (c) SO_2 were removed from the system. The temperature remains constant.

- 10.42 Heating solid sodium bicarbonate in a closed vessel establishes the following equilibrium:



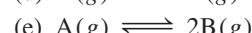
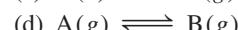
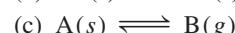
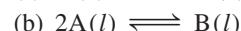
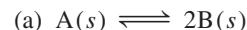
What would happen to the equilibrium position if (a) some of the CO_2 were removed from the system; (b) some solid Na_2CO_3 were added to the system; or (c) some of the solid NaHCO_3 were removed from the system? The temperature remains constant.

- 10.43 Consider the following equilibrium systems:



Predict the change in the equilibrium constant K_P that would occur in each case if the temperature of the reacting system were raised.

- 10.44 What effect does an increase in pressure have on each of the following systems at equilibrium? The temperature is kept constant and, in each case, the reactants are in a cylinder fitted with a movable piston.



- 10.45 Consider the equilibrium



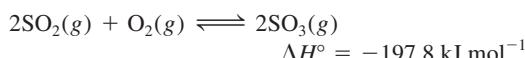
What would be the effect on the position of equilibrium of (a) increasing the total pressure on the system by decreasing its volume; (b) adding I_2 to the reaction mixture; or (c) decreasing the temperature?

- 10.46 Consider the following equilibrium process:



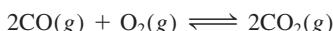
Predict the direction of the shift in equilibrium when (a) the temperature is raised; (b) more chlorine gas is added to the reaction mixture; (c) some PCl_3 is removed from the mixture; or (d) the pressure on the gases is increased.

- 10.47 Consider the reaction



Comment on the changes in the concentrations of SO_2 , O_2 , and SO_3 at equilibrium if we were to (a) increase the temperature; (b) increase the pressure; (c) increase SO_2 ; or (d) add helium at constant volume.

- 10.48 Consider the gas-phase reaction



Predict the shift in the equilibrium position when helium gas is added to the equilibrium mixture (a) at constant pressure and (b) at constant volume.

- 10.49 Consider the following equilibrium reaction in a closed container:



What will happen if (a) the volume is increased; (b) some CaO is added to the mixture; (c) some CaCO_3 is removed; (d) some CO_2 is added to the mixture; (e) a few drops of an NaOH solution are added to the mixture; (f) a few drops of an HCl solution are added to the mixture (ignore the reaction between CO_2 and water); or (g) the temperature is increased?

- 10.50 At a certain temperature and a total pressure of 1.2 bar, the partial pressures of an equilibrium mixture



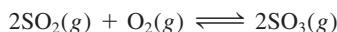
are $P_{\text{A}} = 0.60$ bar and $P_{\text{B}} = 0.60$ bar. (a) Calculate the K_p for the reaction at this temperature. (b) If the total pressure were increased to 1.5 bar, what would be the partial pressures of A and B at equilibrium?

- 10.51 When heated calcium carbonate decomposes according to the reaction



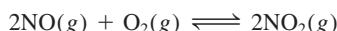
The rate of decomposition is slow until the partial pressure of CO_2 reaches 1 bar. Using the data in Appendix 2, determine the temperature at which the equilibrium partial pressure of CO_2 for this reaction is equal to 1 bar. Assume that ΔS° and ΔH° for this reaction are both temperature independent.

- 10.52 Use the data in Appendix 2 to calculate the equilibrium constant, K_p , for the reaction



at (a) 25°C and (b) 75°C . State any assumptions that you make.

- 10.53 The following table gives the equilibrium constant (K_p) for the reaction



at various temperatures:

| | | | | | |
|---------------|-----|------|-------|--------|--------|
| K_p | 138 | 5.12 | 0.436 | 0.0626 | 0.0130 |
| $T(\text{K})$ | 600 | 700 | 800 | 900 | 1000 |

Determine graphically the standard enthalpy change for this reaction (ΔH°). State any assumptions that you make.

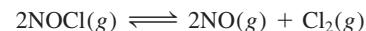
- 10.54 For the reaction



the equilibrium constant K_p is 0.534 at 960 K and 1.571 at 1260 K . From these data, determine the standard enthalpy change (ΔH°) for this reaction. State any assumptions that you make.

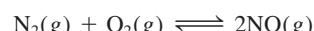
Additional Problems

- 10.55 Consider the statement: "The equilibrium constant of a reacting mixture of solid NH_4Cl and gaseous NH_3 and HCl is 0.316." List three important pieces of information that are missing from this statement.
- 10.56 Pure nitrosyl chloride (NOCl) gas was heated to 240°C in a 1.00-L container. At equilibrium, the total pressure was 1.01 bar and the NOCl pressure was 0.65 bar.



(a) Calculate the partial pressures of NO and Cl_2 in the system. (b) Calculate the equilibrium constant K_p .

- 10.57 The equilibrium constant K_p for the formation of the air pollutant nitric oxide (NO) in an automobile engine at 530°C is 2.9×10^{-11} :



(a) Calculate the partial pressure of NO under these conditions if the partial pressures of nitrogen and oxygen are 3.0 and 0.012 bar, respectively. (b) Repeat the calculation for atmospheric conditions where the partial pressures of nitrogen and oxygen are 0.79 and 0.21 bar, respectively, and the temperature is 25°C . (The K_p for the reaction is 4.0×10^{-31} at this temperature.) (c) Is the formation of NO endothermic or exothermic? (d) What natural phenomenon promotes the formation of NO? Why?

- 10.58 Baking soda (sodium bicarbonate) undergoes thermal decomposition as follows:



Would we obtain more CO_2 and H_2O by adding extra baking soda to the reaction mixture in (a) a closed vessel or (b) an open vessel?

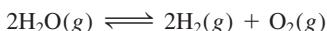
- 10.59 Consider the following reaction at equilibrium:



From the following data, calculate the equilibrium constant (both K_P and K_c) at each temperature. Is the reaction endothermic or exothermic?

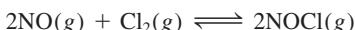
| Temperature (°C) | [A] (M) | [B] (M) |
|------------------|---------|---------|
| 200 | 0.0125 | 0.843 |
| 300 | 0.171 | 0.764 |
| 400 | 0.250 | 0.724 |

- 10.60 The equilibrium constant K_P for the reaction



is 2×10^{-42} at 25°C. (a) What is K_c for the reaction at the same temperature? (b) The very small value of K_P (and K_c) indicates that the reaction overwhelmingly favors the formation of water molecules. Explain why, despite this fact, a mixture of hydrogen and oxygen gases can be kept at room temperature without any change.

- 10.61 Consider the following reacting system:



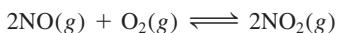
What combination of temperature and pressure would maximize the yield of nitrosyl chloride (NOCl)? [Hint: $\Delta H_f^\circ(\text{NOCl}) = 51.7 \text{ kJ mol}^{-1}$. You will also need to consult Appendix 2.]

- 10.62 The decomposition of ammonium hydrogen sulfide



is an endothermic process. A 6.1589-g sample of the solid is placed in an evacuated 4.000-L vessel at exactly 24°C. After equilibrium has been established, the total pressure inside is 0.732 bar. Some solid NH₄HS remains in the vessel. (a) What is the K_P for the reaction? (b) What percentage of the solid has decomposed? (c) If the volume of the vessel were doubled at constant temperature, what would happen to the amount of solid in the vessel?

- 10.63 Consider the reaction



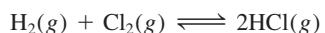
At 430°C, an equilibrium mixture consists of 0.020 mole of O₂, 0.040 mole of NO, and 0.96 mole of NO₂. Calculate K_P for the reaction, given that the total pressure is 0.20 bar.

- 10.64 When heated, ammonium carbamate decomposes as follows:



At a certain temperature, the equilibrium pressure of the system is 0.322 bar. Calculate K_P for the reaction.

- 10.65 A mixture of 0.47 mole of H₂ and 3.59 moles of HCl is heated to 2800°C. Calculate the equilibrium partial pressures of H₂, Cl₂, and HCl if the total pressure is 2.03 bar. For the reaction



K_P is 193 at 2800°C.

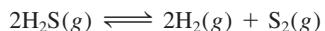
- 10.66 Consider the reaction between NO₂ and N₂O₄ in a closed container:



Initially there is 1 mole of N₂O₄ present. At equilibrium, α mole of N₂O₄ has dissociated to form NO₂. (a) Derive an expression for K_P in terms of α and P , the total pressure. (b) How does the expression in part (a) help you predict the shift in the equilibrium concentrations due to an increase in P ? Does your prediction agree with Le Châtelier's principle?

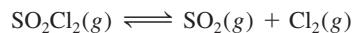
- 10.67 One mole of N₂ and three moles of H₂ are placed in a flask at 375°C. Calculate the total pressure of the system at equilibrium if the mole fraction of NH₃ is 0.21. The K_P for the reaction is 4.37×10^{-1} .

- 10.68 At 1130°C, the equilibrium constant K_c for the reaction

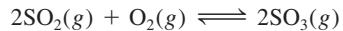


is 2.25×10^{-4} . If [H₂S] = $4.84 \times 10^{-3} \text{ M}$ and [H₂] = $1.50 \times 10^{-3} \text{ M}$, calculate [S₂].

- 10.69 A quantity of 6.75 g of SO₂Cl₂ was placed in a 2.00-L flask. At 648 K, there is 0.0345 mole of SO₂ present. Calculate K_c for the reaction



- 10.70 The formation of SO₃ from SO₂ and O₂ is an intermediate step in the manufacture of sulfuric acid, and it is also responsible for the acid rain phenomenon. The equilibrium constant K_P for the reaction



is 0.13 at 830°C. In one experiment, 2.00 mol SO₂ and 2.00 mol O₂ were initially present in a flask. What must the total pressure at equilibrium be in order to have an 80.0 percent yield of SO₃?

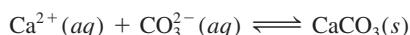
- 10.71 Consider the dissociation of iodine:



A 1.00-g sample of I₂ is heated to 1200°C in a 500-mL flask. At equilibrium the total pressure is 1.53 bar. Calculate K_P for the reaction. (Hint: Use the result in Problem 10.66(a). The degree of dissociation α can be obtained by first calculating

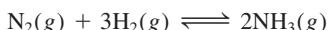
the ratio of observed pressure over calculated pressure, assuming no dissociation.)

- 10.72 Eggshells are composed mostly of calcium carbonate (CaCO_3) formed by the reaction



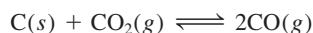
The carbonate ions are supplied by carbon dioxide produced as a result of metabolism. Explain why eggshells are thinner in the summer when the rate of panting by chickens is greater. Suggest a remedy for this situation.

- 10.73 The equilibrium constant K_P for the following reaction is 4.26×10^{-4} at 375°C :



In a certain experiment, a student starts with 0.884 bar of N_2 and 0.383 bar of H_2 in a constant-volume vessel at 375°C . Calculate the partial pressures of all species when equilibrium is reached.

- 10.74 A quantity of 0.20 mole of carbon dioxide was heated to a certain temperature with an excess of graphite in a closed container until the following equilibrium was reached:



Under these conditions, the average molar mass of the gases was 35 g mol^{-1} . (a) Calculate the mole fractions of CO and CO_2 . (b) What is K_P if the total pressure is 11 bar? (Hint: The average molar mass is the sum of the products of the mole fraction of each gas and its molar mass.)

- 10.75 Heated calcium carbonate decomposes according to the reaction



Given that the equilibrium partial pressures of CO_2 at 700°C and 950°C are 22.6 and 1829 mmHg, respectively, determine the standard enthalpy change (ΔH°) for this reaction. State any assumptions that you make.

- 10.76 When dissolved in water, glucose (corn sugar) and fructose (fruit sugar) exist in equilibrium as follows:



A chemist prepared a 0.244 M fructose solution at 25°C . At equilibrium, it was found that its concentration had decreased to 0.113 M . (a) Calculate the equilibrium constant for the reaction. (b) At equilibrium, what percentage of fructose was converted to glucose?

- 10.77 At room temperature, solid iodine is in equilibrium with its vapor through sublimation and deposition. Describe how you would use radioactive iodine, in

either solid or vapor form, to show that there is a dynamic equilibrium between these two phases.

- 10.78 At 1024°C , the pressure of oxygen gas from the decomposition of copper(II) oxide (CuO) is 0.50 bar:



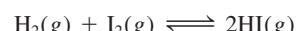
(a) What is K_P for the reaction? (b) Calculate the fraction of CuO that will decompose if 0.16 mole of it is placed in a 2.0-L flask at 1024°C . (c) What would the fraction be if a 1.0-mole sample of CuO were used? (d) What is the smallest amount of CuO (in moles) that would establish the equilibrium?

- 10.79 A mixture containing 3.9 moles of NO and 0.88 mole of CO_2 was allowed to react in a flask at a certain temperature according to the equation



At equilibrium, 0.11 mole of CO_2 was present. Calculate the equilibrium constant K_c of this reaction.

- 10.80 The equilibrium constant K_c for the reaction



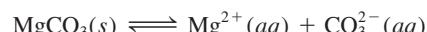
is 54.3 at 430°C . At the start of the reaction, there are 0.714 mole of H_2 , 0.984 mole of I_2 , and 0.886 mole of HI in a 2.40-L reaction chamber. Calculate the concentrations of the gases at equilibrium.

- 10.81 When heated, a gaseous compound A dissociates as follows:



In an experiment, A was heated at a certain temperature until its equilibrium pressure reached $0.14P$, where P is the total pressure in bar. Calculate the equilibrium constant K_P of this reaction.

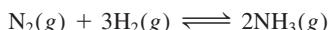
- 10.82 The solubility of the salt MgCO_3 is governed by the following equilibrium equation:



The equilibrium constant K for this reaction is 6.8×10^{-6} at 25°C . Use the data in Appendix 2 to determine K for this reaction at 75°C .

- 10.83 When a gas was heated under atmospheric conditions, its color deepened. Heating above 150°C caused the color to fade, and at 550°C the color was barely detectable. However, at 550°C , the color was partially restored by increasing the pressure of the system. Which of the following best fits the preceding description? Justify your choice. (a) A mixture of hydrogen and bromine, (b) pure bromine, or (c) a mixture of nitrogen dioxide and dinitrogen tetroxide. (Hint: Bromine has a reddish color and nitrogen dioxide is a brown gas. The other gases are colorless.)

- 10.84 The equilibrium constant K_c for the following reaction is 1.2 at 375°C:



- (a) What is the value of K_p for this reaction?
- (b) What is the value of the equilibrium constant K_c for $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$?
- (c) What is K_c for $\text{N}_2(g) + \text{H}_2(g) \rightleftharpoons \text{NH}_3(g)$?
- (d) What are the values of K_p for the reactions described in parts (b) and (c)?

- 10.85 A sealed glass bulb contains a mixture of NO_2 and N_2O_4 gases. Describe what happens to the following properties of the gases when the bulb is heated from 20°C to 40°C: (a) color, (b) pressure, (c) average molar mass, (d) degree of dissociation (from N_2O_4 to NO_2), and (e) density. Assume that volume remains constant.
(Hint: NO_2 is a brown gas; N_2O_4 is colorless.)

- 10.86 At 20°C, the vapor pressure of water is 0.0234 bar. Calculate K_p and K_c for the process



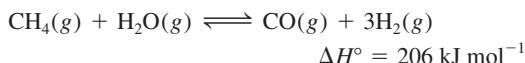
- 10.87 Industrially, sodium metal is obtained by electrolyzing molten sodium chloride. The reaction at the cathode is $\text{Na}^+ + e^- \longrightarrow \text{Na}$. We might expect that potassium metal would also be prepared by electrolyzing molten potassium chloride. However, potassium metal is soluble in molten potassium chloride and therefore is hard to recover. Furthermore, potassium vaporizes readily at the operating temperature, creating hazardous conditions. Instead, potassium is prepared by the distillation of molten potassium chloride in the presence of sodium vapor at 892°C:



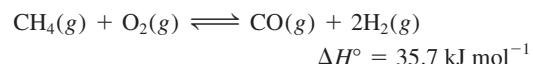
In view of the fact that potassium is a stronger reducing agent than sodium, explain why this approach works. (The boiling points of sodium and potassium are 892°C and 770°C, respectively.)

- 10.88 In the gas phase, nitrogen dioxide is actually a mixture of nitrogen dioxide (NO_2) and dinitrogen tetroxide (N_2O_4). If the density of such a mixture is 2.3 g L⁻¹ at 74°C and 1.3 bar, calculate the partial pressures of the gases and K_p for the dissociation of N_2O_4 .

- 10.89 About 75 percent of hydrogen for industrial use is produced by the *steam-reforming* process. This process is carried out in two stages called primary and secondary reforming. In the primary stage, a mixture of steam and methane at about 30 bar is heated over a nickel catalyst at 800°C to give hydrogen and carbon monoxide:

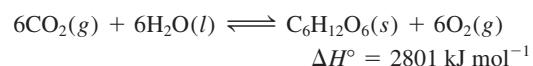


The secondary stage is carried out at about 1000°C, in the presence of air, to convert the remaining methane to hydrogen:



- (a) What conditions of temperature and pressure would favor the formation of products in both the primary and secondary stage? (b) The equilibrium constant K_c for the primary stage is 18 at 800°C. (i) Calculate K_p for the reaction. (ii) If the partial pressures of methane and steam were both 15 bar at the start, what are the pressures of all the gases at equilibrium?

- 10.90 Photosynthesis can be represented by



Explain how the equilibrium would be affected by the following changes: (a) partial pressure of CO_2 is increased, (b) O_2 is removed from the mixture, (c) $\text{C}_6\text{H}_{12}\text{O}_6$ (glucose) is removed from the mixture, (d) more water is added, or (e) temperature is decreased.

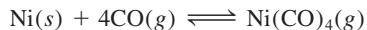
- 10.91 Consider the decomposition of ammonium chloride at a certain temperature:



Calculate the equilibrium constant K_p if the total pressure is 2.2 bar at that temperature.

- 10.92 At 25°C, the equilibrium partial pressures of NO_2 and N_2O_4 are 0.15 and 0.20 bar, respectively. If the volume is doubled at constant temperature, calculate the partial pressures of the gases when a new equilibrium is established.

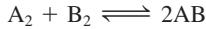
- 10.93 In 1899, the German chemist Ludwig Mond developed a process for purifying nickel by converting it to the volatile nickel tetracarbonyl $[\text{Ni}(\text{CO})_4]$ (b.p. 42.2°C):



- (a) Describe how you can separate nickel and its solid impurities. (b) How would you recover nickel? [ΔH_f° for $\text{Ni}(\text{CO})_4$ is $-602.9 \text{ kJ mol}^{-1}$.]

- 10.94 Consider the equilibrium reaction described in Problem 10.11. A quantity of 2.50 g of PCl_5 is placed in an evacuated 0.500-L flask and heated to 250°C. (a) Calculate the pressure of PCl_5 , assuming it does not dissociate. (b) Calculate the partial pressure of PCl_5 at equilibrium. (c) What is the total pressure at equilibrium? (d) What is the degree of dissociation of PCl_5 ? (The degree of dissociation is given by the fraction of PCl_5 that has undergone dissociation.)

- 10.95 Consider the equilibrium system $3A \rightleftharpoons B$. Sketch the changes in the concentrations of A and B over time for the following situations: (a) initially only A is present; (b) initially only B is present; and (c) initially both A and B are present (with A in higher concentration). In each case, assume that the concentration of B is higher than that of A at equilibrium.
- 10.96 The vapor pressure of mercury is 0.0020 mmHg at 26°C. (a) Calculate K_c and K_p for the process $Hg(l) \rightleftharpoons Hg(g)$. (b) A chemist breaks a thermometer measuring 6.1 m long, 5.3 m wide, and 3.1 m high and spills mercury onto the floor of a laboratory. Calculate the mass of mercury (in grams) vaporized at equilibrium and the concentration of mercury vapor in mg m^{-3} . Does this concentration exceed the safety limit of 0.05 mg m^{-3} ? (Ignore the volume of furniture and other objects in the laboratory.)
- 10.97 At 25°C, a mixture of NO_2 and N_2O_4 gases are in equilibrium in a cylinder fitted with a movable piston. The concentrations are $[\text{NO}_2] = 0.0475 M$ and $[\text{N}_2\text{O}_4] = 0.487 M$. The volume of the gas mixture is halved by pushing down on the piston at constant temperature. Calculate the concentrations of the gases when equilibrium is reestablished. Will the color become darker or lighter after the change? (Hint: K_c for the dissociation of N_2O_4 is 4.63×10^{-3} . $\text{N}_2\text{O}_4(g)$ is colorless, and $\text{NO}_2(g)$ has a brown color.)
- 10.98 A student placed a few ice cubes in a drinking glass with water. A few minutes later, she noticed that some of the ice cubes were fused together. Explain what happened.
- 10.99 The K_p for the reaction
- $$\text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2 + \text{Cl}_2(g)$$
- is 2.07 at 648 K. A sample of SO_2Cl_2 is placed in a container and heated to 648 K while the total pressure is kept constant at 9.00 bar. Calculate the partial pressures of the gases at equilibrium.
- 10.100 The equilibrium constant K_c for the reaction
- $$2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$$
- is 0.83 at 375°C. A 14.6-g sample of ammonia is placed in a 4.00-L flask and heated to 375°C. Calculate the concentrations of all the gases when equilibrium is reached.
- 10.101 Consider the following reaction at a certain temperature:



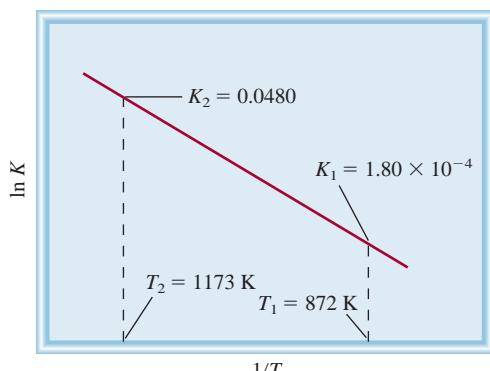
The mixing of 1 mole of A_2 with 3 moles of B_2 gives rise to x moles of AB at equilibrium. The addition of 2 more moles of A_2 produces another x moles of AB . What is the equilibrium constant for the reaction?

- 10.102 The van't Hoff equation for the temperature dependence of equilibrium constants (Equation 10.16) is very similar in form to the Clausius-Clapeyron equation (Equation 9.4) for the temperature dependence of vapor pressure. Give an explanation for this similarity. (Hint: Write the process of vaporization of a liquid as an equilibrium reaction. What is the equilibrium constant?)
- 10.103 Iodine is sparingly soluble in water but is much more soluble in carbon tetrachloride (CCl_4). The equilibrium constant, also called the partition coefficient, for the distribution of I_2 between these two phases
- $$\text{I}_2(aq) \rightleftharpoons \text{I}_2(\text{CCl}_4)$$
- is 83 at 20°C. (a) A student adds 0.030 L of CCl_4 to 0.200 L of an aqueous solution containing 0.032 g I_2 . The mixture is shaken, and the two phases are then allowed to separate. Calculate the fraction of I_2 remaining in the aqueous phase. (b) The student now repeats the extraction of I_2 with another 0.030 L of CCl_4 . Calculate the fraction of the I_2 from the original solution that remains in the aqueous phase. (c) Compare the result in part (b) with a single extraction using 0.060 L of CCl_4 . Comment on the difference.

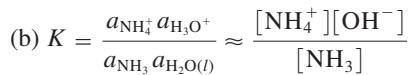
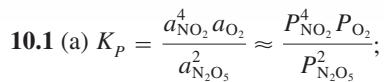
- 10.104 The following diagram shows the variation of the equilibrium constant with temperature for the reaction



Calculate ΔG° , ΔH° , and ΔS° for the reaction at 872 K.



Answers to Practice Exercises



10.2 $K_c = 2.2 \times 10^2$; $K_P = 7.6$ **10.3** $K_P = 0.0718$; $K_c = 6.7 \times 10^{-5}$ **10.4** 9.5×10^{-17} **10.5** $Q > K$, so the reaction proceeds from right to left (towards reactants). **10.6** $[\text{Br}_2] = 0.065 \text{ M}$, $[\text{Br}] = 8.4 \times 10^{-3} \text{ M}$. **10.7** $P_{\text{NH}_3} = P_{\text{H}_2\text{S}} = 0.268 \text{ bar}$; 15.8 g of $\text{NH}_4\text{HS}(s)$ remain in the container. **10.8** 1.6×10^{57}

10.9 33 kJ mol^{-1} **10.10** $\Delta G_{\text{rxn}} = 1.87 \text{ kJ mol}^{-1} > 0$, so the reaction will proceed from right to left (toward reactants).

10.11 (a) Reaction will shift toward products (left to right). (b) $Q_P = 3.1 \times 10^4 < K_P$ indicating that the reaction will shift toward products, as seen in part (a). **10.12** The reaction shifts from left to right (toward products). **10.13** (a) $x_{\text{PCl}_3} = x_{\text{Cl}_2} = 0.350$, $x_{\text{PCl}_5} = 0.300$, (b) $x_{\text{PCl}_3} = x_{\text{Cl}_2} = 0.191$, $x_{\text{PCl}_5} = 0.612$; at higher pressure, the reaction shifts toward the reactant, which is consistent with Le Châtelier's principle because $\Delta n = 1 > 0$. **10.14** 329 K

11

Chapter

Acids and Bases

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Some of the most important processes in chemical and biological systems are acid-base reactions in aqueous solutions. In this chapter on the properties of acids and bases, we will study the definitions of acids and bases, the pH scale, the ionization of weak acids and weak bases, and the relationship between acid strength and molecular structure. We will also look at oxides that can act as acids and bases.

11.1 | Many Processes in Chemistry Are Acid-Base Reactions

Common acids and bases include aspirin (acetylsalicylic acid) and milk of magnesia (magnesium hydroxide). Besides providing the basis of many medicinal and household products, though, acid-base chemistry is important in industrial processes and essential in sustaining biological systems. Before we can discuss acid-base reactions, we need to know more about acids and bases themselves.

Arrhenius Definition of Acids and Bases

The first definitions of acids and bases were formulated in the late nineteenth century by the Swedish chemist Svante Arrhenius.¹ According to Arrhenius, an *acid* is a substance that yields hydrogen ions (H^+) when dissolved in water. For example, HCl fits the Arrhenius definition of an acid because, when dissolved in water, HCl dissociates into $H^+(aq)$ and $Cl^-(aq)$:



Arrhenius defined a *base*, on the other hand, as a substance that yields hydroxide ions (OH^-) when dissolved in water. For example, when sodium hydroxide is dissolved in water, it dissociates into $\text{Na}^+(aq)$ and $OH^-(aq)$



so NaOH fits the Arrhenius definition of a base.

Acids have a number of distinguishing properties:

- ▶ Acids taste sour; vinegar, for example, owes its sour taste to acetic acid, whereas lemons and other citrus fruits owe theirs to citric acid.
- ▶ Acids cause color changes in plant dyes, for example, they change the color of litmus from blue to red.
- ▶ Acids react with certain metals, such as zinc, magnesium, and iron, to produce hydrogen gas. A typical reaction is that between hydrochloric acid and magnesium:



- ▶ Acids react with carbonates and bicarbonates, such as Na_2CO_3 , CaCO_3 , and NaHCO_3 , to produce carbon dioxide gas. Figure 11.1 shows the reaction between hydrochloric acid and CaCO_3 (in the form of chalk):



- ▶ Aqueous acid solutions conduct electricity.

In contrast, bases have the following characteristic properties:

- ▶ Bases taste bitter.
- ▶ Bases feel slippery; soaps, for example, which contain bases, are slippery.
- ▶ Bases cause color changes in plant dyes, for example, they change the color of litmus from red to blue.
- ▶ Aqueous base solutions conduct electricity.



Figure 11.1 A piece of blackboard chalk, which is mostly CaCO_3 , reacts with hydrochloric acid.

1. Svante August Arrhenius (1859–1927). Swedish chemist. Arrhenius made important contributions in the study of chemical kinetics and electrolyte solutions. He also speculated that life had come to Earth from other planets, a theory now known as *panspermia*. Arrhenius was awarded the Nobel Prize in Chemistry in 1903.

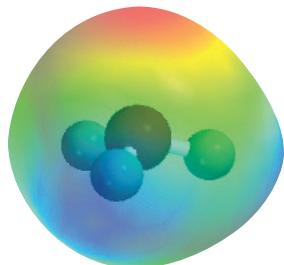
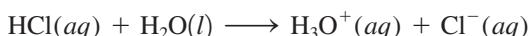
Brønsted Definition of Acids and Bases

Arrhenius's definitions of acids and bases are limited because they apply only to aqueous solutions. Broader definitions were proposed by the Danish chemist Johannes Brønsted² in 1932; a **Brønsted acid** is a proton donor, and a **Brønsted base** is a proton acceptor. These definitions do not require acids and bases to be in aqueous solution, just that acids donate a proton and bases accept one.

Hydrochloric acid is a Brønsted acid because it donates a proton in water:



The H^+ ion is a hydrogen atom that has lost its electron, that is, it is just a bare proton. The size of a proton is about 10^{-15} m, compared to a diameter of 10^{-10} m for an average atom or ion. Such an exceedingly small charged particle cannot exist as a separate entity in aqueous solution owing to its strong attraction for the negative pole (the O atom) in H_2O . Consequently, the proton exists in the hydrated form as shown in Figure 11.2, and therefore the ionization of hydrochloric acid should be written as

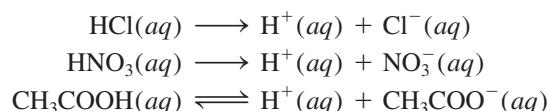


Electrostatic potential map of the H_3O^+ ion. In the rainbow color spectrum representation, the most electron-rich region is red and the most electron-poor region is blue.

In reality, no acids are known to ionize completely in water.

The *hydrated proton* (H_3O^+) is called the **hydronium ion**. This equation shows a reaction in which a Brønsted acid (HCl) donates a proton to a Brønsted base (H_2O). Experiments show that the hydronium ion is further hydrated, so the proton may have several water molecules associated with it. Because the acidic properties of the proton are unaffected by the degree of hydration, in this text we will often use $\text{H}^+(aq)$ to represent the hydrated proton. This notation is for convenience, but H_3O^+ is closer to reality. Keep in mind that both notations represent the same species in aqueous solution.

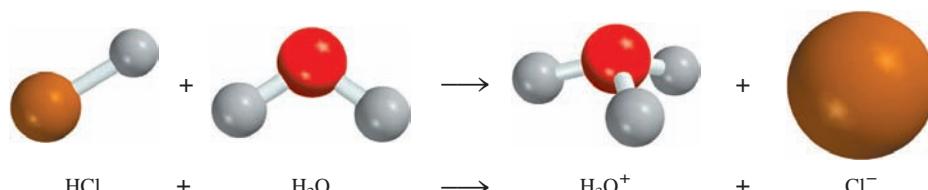
Acids commonly used in the laboratory include hydrochloric acid (HCl), nitric acid (HNO_3), acetic acid (CH_3COOH), sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4). The first three are **monoprotic acids**, that is, *each unit of the acid yields one hydrogen ion upon ionization*:



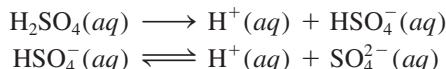
The double arrow in the acetic acid ionization reaction indicates that the dissociation is incomplete, that is, a certain amount of undissociated acetic acid exists in solution with the dissociated acetic acid. Acetic acid is called a **weak acid** because it *ionizes only to a limited extent in water*. HCl and HNO_3 are **strong acids** because they are, *for all practical purposes, completely ionized in water*. The relative strengths of acids and bases are discussed in detail in Section 11.2.

2. Johannes Nicolaus Brønsted (1879–1947). Danish chemist. In addition to his theory of acids and bases, Brønsted worked on thermodynamics and the separation of mercury into isotopes.

Figure 11.2 The ionization of HCl in water to form the hydronium ion and the chloride ion.

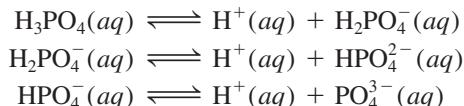


Sulfuric acid (H_2SO_4) is a **diprotic acid** because *each unit of the acid can give up two H^+ ions*, in two separate steps:



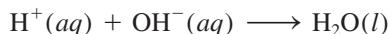
H_2SO_4 is a strong acid (the first step of ionization is complete), but HSO_4^- is a weak acid or weak electrolyte, so we use a double arrow to represent its incomplete ionization.

Triprotic acids, which *yield three H^+ ions*, are relatively few in number. The best-known triprotic acid is phosphoric acid, whose ionizations are



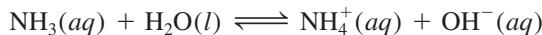
All three species (H_3PO_4 , H_2PO_4^- , and HPO_4^{2-}) are weak acids, so we use the double arrows to represent each ionization step. Anions such as H_2PO_4^- and HPO_4^{2-} are found in aqueous solutions of phosphates such as NaH_2PO_4 and Na_2HPO_4 .

The hydroxide ion (OH^-) is classified as a Brønsted base because it can accept a proton as follows:

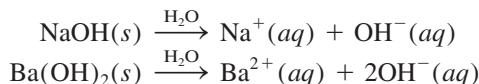


Thus, any Arrhenius base (that is, any substance that yields hydroxide ions in solution) can be classified as a Brønsted base.

Ammonia (NH_3), which is not an Arrhenius base, is nevertheless classified as a Brønsted base because it can accept an H^+ ion from water (Figure 11.3):



Ammonia is a **weak base** because only a small fraction of dissolved NH_3 molecules react with water to form NH_4^+ and OH^- ions. In contrast, sodium hydroxide and barium hydroxide are **strong bases** because they completely ionize in solution:



The most commonly used strong base in the laboratory is sodium hydroxide. It is inexpensive and water soluble. (In fact, all the alkali metal hydroxides are water soluble.) The most commonly used weak base is aqueous ammonia solution, which is sometimes erroneously called ammonium hydroxide; there is no evidence that the species NH_4OH actually exists. All the Group 2A elements form hydroxides of the



Zn reacts more vigorously with a strong acid like HCl (left) than with a weak acid like CH_3COOH (right) of the same concentration because there are more H^+ ions in the former solution.

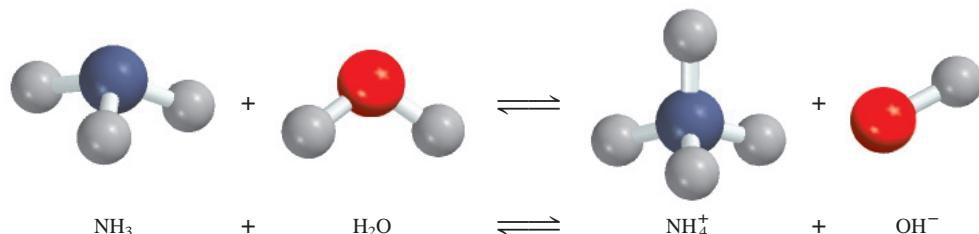


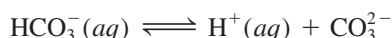
Figure 11.3 The ionization of ammonia in water to form the ammonium ion and the hydroxide ion.



Note that this bottle of aqueous ammonia is erroneously labeled.

type $M(OH)_2$, where M denotes an alkaline earth metal. Of these hydroxides, only $Ba(OH)_2$ is water soluble. Magnesium and calcium hydroxides are used in medicine and industry. Hydroxides of other metals, such as $Al(OH)_3$ and $Zn(OH)_2$, are insoluble in water and are not used as bases.

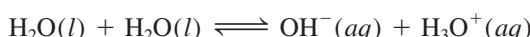
Many substances can act as both a Brønsted acid and a Brønsted base and are called **amphoteric**. For example, the bicarbonate ion is a Brønsted acid because it ionizes in aqueous solution to yield a proton and the carbonate ion:



It is also a Brønsted base because it can accept a proton to form carbonic acid:



Water is amphoteric, too, because it can donate a proton to another water molecule:



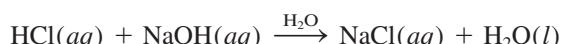
Thus, the water molecule that donates the proton, acts as a Brønsted acid, whereas the water molecule that accepts the proton acts as a Brønsted base.

Acid-Base Neutralization

A **neutralization reaction** is a reaction between an acid and a base. Aqueous acid-base reactions generally produce water and a **salt**, which is an ionic compound made up of a cation other than H^+ and an anion other than OH^- or O_2^- :

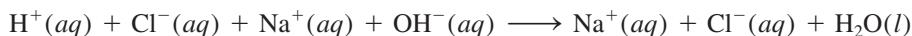


All salts (such as table salt, $NaCl$) are **strong electrolytes**, because they, for all practical purposes, completely ionize in aqueous solution. $NaCl$ is produced in the neutralization reaction between HCl and $NaOH$:

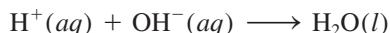


Acid-base neutralization reactions generally go to completion.

However, because both the acid and the base are strong electrolytes, they are completely dissociated into ions in solution. The ionic equation is



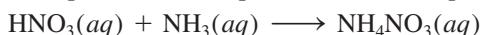
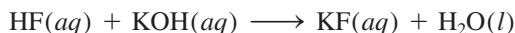
Therefore, the reaction can be represented by the net ionic equation:



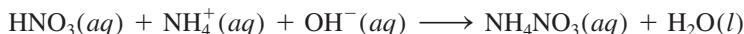
because both Na^+ and Cl^- are **spectator ions**, that is, they do not appear in the net equation.

If we had started the preceding reaction with equal molar amounts of the acid and the base, at the end of the reaction we would have only the salt and water, with no leftover acid or base. This is a characteristic of acid-base neutralization reactions.

The following are other examples of acid-base neutralization reactions, represented by molecular equations:

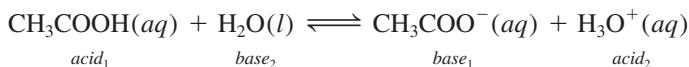


The last equation looks different because it does not show water as a product. However, if we express $\text{NH}_3(aq)$ as $\text{NH}_4^+(aq)$ and $\text{OH}^-(aq)$, as discussed previously, then the equation becomes



Conjugate Acid-Base Pairs

The concept of the **conjugate acid-base pair**, which can be defined as *an acid and its conjugate base or a base and its conjugate acid*, arises from the Brønsted definition of acids and bases. The conjugate base of a Brønsted acid is the species that remains after the acid donates a proton. Conversely, a conjugate acid results from the addition of a proton to a Brønsted base. Every Brønsted acid has a conjugate base, and every Brønsted base has a conjugate acid. For example, the chloride ion (Cl^-) is the conjugate base formed from the acid HCl , and H_2O is the conjugate base of the acid H_3O^+ (the hydronium ion). Similarly, the ionization of acetic acid can be represented as



The subscripts 1 and 2 designate the two conjugate acid-base pairs. In other words, the acetate ion (CH_3COO^-) is the conjugate base of CH_3COOH and H_3O^+ is the conjugate acid of H_2O . Both the ionization of HCl and the ionization of CH_3COOH are examples of Brønsted acid-base reactions.

In Example 11.1 we practice identifying the conjugate pairs in an acid-base reaction.

The word *conjugate* means “joined together.”

Example 11.1

Identify the conjugate acid-base pairs in the reaction between ammonia and hydrofluoric acid in aqueous solution



Strategy A conjugate base always has one fewer H atom and one more negative charge (or one fewer positive charge) than the formula of the corresponding acid. Similarly, a conjugate acid has one more H atom and one more positive charge (or one fewer negative charge) than the formula of the corresponding base.

Solution NH_3 has one fewer H atom and one fewer positive charge than NH_4^+ , whereas F^- has one fewer H atom and one more negative charge than HF . Therefore, the conjugate acid-base pairs are (1) NH_4^+ and NH_3 and (2) HF and F^- .

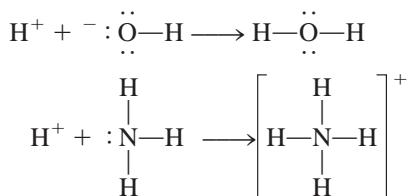
Practice Exercise Identify the conjugate acid-base pairs for the reaction



It is acceptable to represent the proton in aqueous solution either as H^+ or as H_3O^+ . The formula H^+ is less cumbersome in calculations involving hydrogen ion concentrations and in calculations involving equilibrium constants. On the other hand, H_3O^+ is more useful in a discussion of Brønsted acid-base properties.

Lewis Definition of Acids and Bases

According to the Brønsted theory, a base must be able to accept protons. By this definition, both the hydroxide ion and ammonia are Brønsted bases:



In each case, the atom to which the proton becomes attached possesses at least one unshared pair of electrons. This characteristic property of OH^- , NH_3 , and other Brønsted bases suggests a more general definition of acids and bases.

In 1932 the American chemist G. N. Lewis formulated such a definition (see Section 3.4). He defined what we now call a **Lewis base** as a substance that can donate a pair of electrons. A **Lewis acid** is a substance that can accept a pair of electrons. For example, in the protonation of ammonia, NH_3 acts as a Lewis base because it donates a pair of electrons to the proton H^+ , which acts as a Lewis acid by accepting the pair of electrons. A Lewis acid-base reaction, therefore, is one that involves the donation of a pair of electrons from one species to another. Such a reaction does not necessarily produce a salt and water.

The significance of the Lewis concept is that it is more general than the Arrhenius or Brønsted definitions. Lewis acid-base reactions include many reactions that do not involve Brønsted acids. Consider, for example, the reaction between boron trifluoride (BF_3) and ammonia to form an adduct compound (Figure 11.4):

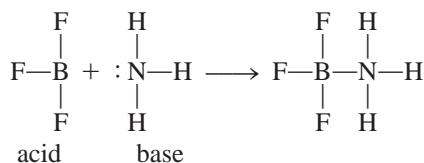
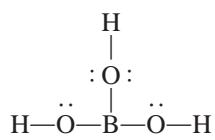


Figure 11.4 A Lewis acid-base reaction involving BF_3 and NH_3 .

A coordinate covalent bond (see page 197) is always formed in a Lewis acid-base reaction.

In Section 3.4, we saw that the B atom in BF_3 is sp^2 -hybridized. The vacant, unhybridized $2p_z$ orbital accepts a pair of electrons from NH_3 . So BF_3 functions as an acid according to the Lewis definition, even though it does not contain an ionizable proton. A coordinate covalent bond (see Section 3.4) is formed between the B and N atoms, as is the case in all Lewis acid-base reactions.

Another Lewis acid containing boron is boric acid. Boric acid (a weak acid used in eyewash) is an oxoacid with the following structure:

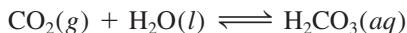


Boric acid does not ionize in water to produce an H^+ ion. Its reaction with water is

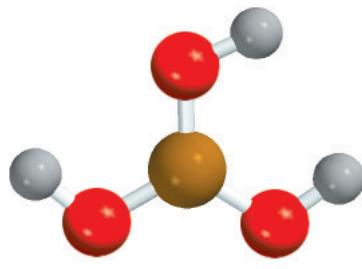
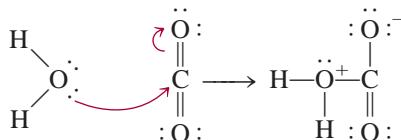


In this Lewis acid-base reaction, boric acid accepts a pair of electrons from the hydroxide ion that is derived from the H_2O molecule.

The hydration of carbon dioxide to produce carbonic acid

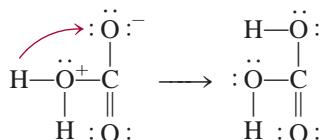


can be understood in the Lewis framework as follows: The first step involves donation of a lone pair on the oxygen atom in H_2O to the carbon atom in CO_2 . An orbital is vacated on the C atom to accommodate the lone pair by removal of the electron pair in the C—O π bond. These shifts of electrons are indicated by the curved arrows.

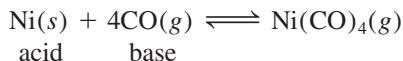
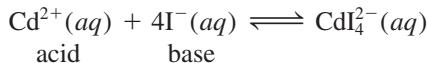
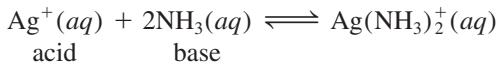


H_3BO_3

Therefore, H_2O is a Lewis base and CO_2 is a Lewis acid. Next, a proton is transferred onto the O atom bearing a negative charge to form H_2CO_3 .



Other examples of Lewis acid-base reactions are



The hydration of metal ions in aqueous solution is in itself a Lewis acid-base reaction. Thus, when copper(II) sulfate (CuSO_4) dissolves in water, each Cu^{2+} ion is associated with six water molecules as $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. In this case, the Cu^{2+} ion acts as the acid and the H_2O molecules act as the base.

Although the Lewis definition of acids and bases has greater significance because of its generality, we normally speak of “an acid” and “a base” in terms of the Brønsted definition. The term “Lewis acid” usually is reserved for substances that can accept a pair of electrons, but do not contain ionizable hydrogen atoms. Example 11.2 shows how to classify compounds as Lewis acids or Lewis bases.

Example 11.2

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

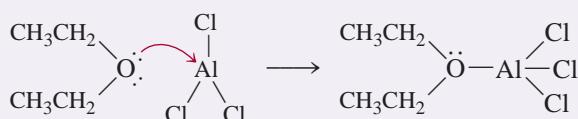
- (a) $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{AlCl}_3 \rightleftharpoons (\text{C}_2\text{H}_5)_2\text{OAlCl}_3$
- (b) $\text{Hg}^{2+}(aq) + 4\text{CN}^-(aq) \rightleftharpoons \text{Hg}(\text{CN})_4^-(aq)$

—Continued

Continued—

Strategy In Lewis acid-base reactions, the acid (which accepts a lone pair of electrons) is usually a cation or an electron-deficient molecule, whereas the base (which donates a lone pair of electrons) is an anion or a molecule containing an atom with lone pairs. (a) Draw the Lewis structure for $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ to see if it can donate or accept a lone pair of electrons. What is the hybridization state of Al in AlCl_3 ? Can it donate or accept a lone pair of electrons? (b) Which ion is likely to be an electron acceptor? An electron donor?

Solution (a) The Al is sp^2 hybridized in AlCl_3 with an empty $2p_z$ orbital. It is electron deficient, sharing only six electrons. Therefore, the Al atom has a tendency to gain two electrons to complete its octet. This property makes AlCl_3 a Lewis acid. On the other hand, the lone pairs on the oxygen atom in $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ make the compound a Lewis base:



(b) Here the Hg^{2+} ion accepts four pairs of electrons from the CN^- ions. Therefore, Hg^{2+} is the Lewis acid and CN^- is the Lewis base.

Practice Exercise Identify the Lewis acid and Lewis base in the reactions

- $\text{Co}^{3+}(aq) + 6\text{NH}_3(aq) \rightleftharpoons \text{Co}(\text{NH}_3)_6^{3+}$
- $\text{CO} + \text{BH}_3 \rightleftharpoons \text{BH}_3\text{CO}$

11.2 | The Acid-Base Properties of Aqueous Solutions Are Governed by the Autoionization Equilibrium of Water

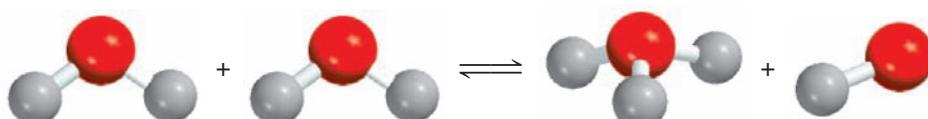
Water is amphoteric and can act either as an acid or as a base. Water functions as a base in reactions with acids such as HCl and CH_3COOH , and it functions as an acid in reactions with bases such as NH_3 . Water is a very weak electrolyte and therefore a poor conductor of electricity, but it does undergo ionization to a small extent:



This reaction is sometimes called the *autoionization of water* (Figure 11.5). The acid-base conjugate pairs are (1) H_2O (acid) and OH^- (base) and (2) H_3O^+ (acid) and H_2O (base).

Tap water and water from underground sources do conduct electricity because they contain many dissolved ions.

Figure 11.5 The reaction between two water molecules to form hydronium and hydroxide ions.



The Ion Product of Water

In the study of acid-base reactions in aqueous solution, the hydrogen ion concentration is key; its value indicates the acidity or basicity of the solution. Therefore, the equilibrium constant for the autoionization of water, according to Equation 9.2, is

$$K = \frac{a_{\text{H}_3\text{O}^{+}(aq)} a_{\text{OH}^{-}(aq)}}{a_{\text{H}_2\text{O}(l)}^2} \quad (11.2)$$

As discussed in Section 10.1, if the H_3O^{+} and OH^{-} concentrations are sufficiently small ($< 0.05 \text{ M}$) then the activities of these solute species are to a good approximation equal to their concentrations, relative to the standard concentration, $c_0 = 1 \text{ M}$. The activity of the nearly pure solvent (H_2O) can be taken to be 1 (Equation 10.5). As a result, the equilibrium constant for the autoionization of water (Equation 11.2) can be expressed³ as

$$K_w = [\text{H}^+] [\text{OH}^-] \quad (11.3)$$

where, for simplicity, we use H^+ to represent H_3O^{+} and where we have added the subscript “w” to represent “water.” The constant K_w is called the **ion-product constant**, which is *the product of the molar concentrations of H^+ and OH^- ions at a particular temperature.*

In pure water at 25°C , the concentrations of H^+ and OH^- ions are equal and found to be $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$. Thus, from Equation 11.3, at 25°C

$$K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

If you could randomly remove and examine 10 particles (H_2O , H^+ , or OH^-) per second from a liter of water, it would take you two years, working nonstop to find one H^+ ion.

Whether we have pure water or an aqueous solution of dissolved species, the following relation *always* holds at 25°C :

$$K_w = [\text{H}^+] [\text{OH}^-] = 1.00 \times 10^{-14}$$

Whenever $[\text{H}^+] = [\text{OH}^-]$, the aqueous solution is said to be neutral. In an acidic solution, there is an excess of H^+ ions and $[\text{H}^+] > [\text{OH}^-]$. In a basic solution, there is an excess of hydroxide ions, so $[\text{H}^+] < [\text{OH}^-]$. In practice, we can change the concentration of either H^+ or OH^- ions in solution, but we cannot vary both of them independently. If we adjust the solution so that $[\text{H}^+] = 1.0 \times 10^{-6} \text{ M}$, the OH^- concentration *must* change to

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.00 \times 10^{-14}}{1.0 \times 10^{-6}} = 1.0 \times 10^{-8} \text{ M}$$

Equation 11.3 assumes that the solution is sufficiently dilute that it can be considered to be ideal. For more concentrated solutions ($> 0.05 \text{ M}$ for singly charged species), ion-pair formation and other types of intermolecular interactions can lead to nonideal solution behavior, and the ion activities (“effective concentrations”) that go into Equation 11.2 will differ somewhat from the molarities. In that case, concentrations calculated from Equation 11.3 will deviate from the actual concentrations in the solution.

3. It is important to note that K_w is a dimensionless constant and that the actual expression (Equation 11.3) should be written

$$K_w = ([\text{H}^+]/c_0) ([\text{OH}^-]/c_0)$$

where $c_0 = 1 \text{ M}$. For simplicity, we have omitted c_0 from the expression. Therefore, we must always be careful to convert the concentration units to M before using Equation 11.3.

However, for most purposes, it is acceptable to ignore these deviations from ideality. In most cases, therefore, this approach will closely approximate the chemical processes that actually take place in the solution phase.

An application of Equation 11.3 is presented in Example 11.3.

Example 11.3

The concentration of OH^- ions in a certain household ammonia cleaning solution is 0.0025 M . Calculate the concentration of H^+ ions.

Solution Rearranging Equation 11.3, we write

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{0.0025} = 4.0 \times 10^{-12}\text{ M}$$

Check Because $[\text{H}^+] < [\text{OH}^-]$, the solution is basic, as we would expect from the earlier discussion of the reaction of ammonia with water.

Practice Exercise Calculate the concentration of OH^- ions in an HCl solution whose hydrogen ion concentration is $1.3 \times 10^{-4}\text{ M}$.

pH—A Measure of Acidity

Because the concentrations of H^+ and OH^- ions in aqueous solutions are frequently very small numbers and therefore inconvenient to work with, Soren Sorensen⁴ in 1909 proposed a more practical measure called pH. The **pH** of a solution is defined as *the negative logarithm (base 10) of the hydrogen ion activity*:

$$\text{pH} \doteq -\log_{10} a_{\text{H}_3\text{O}^+} \quad \text{or} \quad \text{pH} \doteq -\log_{10} a_{\text{H}^+} \quad (11.4)$$

For dilute solutions in which the activity of the hydrogen ion can be well approximated by its concentration relative to the standard concentration, we have

$$\text{pH} = -\log_{10} a_{\text{H}^+} \approx -\log_{10} [\text{H}^+] \quad (11.5)$$

The pH of concentrated acid solutions can be negative. For example, the pH of a 2.0 M HCl solution is approximately -0.3 .

where $[\text{H}^+]$ is understood to be the *numerical* value of the hydrogen ion concentration in mol L^{-1} (without units). Equation 11.4 is simply a definition designed to give us convenient numbers to work with. The negative logarithm gives us a positive number for pH, which otherwise would be negative for most solutions due to the small value of $[\text{H}^+]$. Like the equilibrium constant, the pH of a solution is a dimensionless quantity.

Because pH is simply a way to express hydrogen ion concentration, acidic and basic solutions at 25°C can be distinguished by their pH values as follows:

Acidic solutions: $[\text{H}^+] > 1.00 \times 10^{-7}\text{ M}$, $\text{pH} < 7.00$

Basic solutions: $[\text{H}^+] < 1.00 \times 10^{-7}\text{ M}$, $\text{pH} > 7.00$

Neutral solutions: $[\text{H}^+] = 1.00 \times 10^{-7}\text{ M}$, $\text{pH} = 7.00$

Thus, pH increases as $[\text{H}^+]$ decreases.

4. Soren Peer Lauritz Sorensen (1868–1939). Danish biochemist. Sorensen originally wrote the symbol as p_H and called p the “hydrogen ion exponent” (*Wasserstoffionexponent*); it is the initial letter of *Potenz* (German), *puissance* (French), and *power* (English). It is now customary to write the symbol as pH.

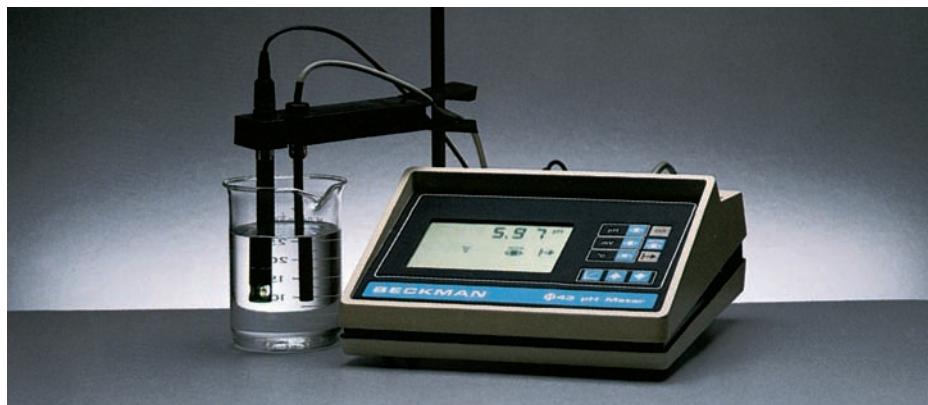


Figure 11.6 A pH meter is commonly used in the laboratory to determine the pH of a solution. Although many pH meters have scales marked with values from 1 to 14, pH values can, in fact, be less than 1 and greater than 14. The science behind the pH meter will be discussed in Chapter 13.

In the laboratory, the pH of a solution is measured with a pH meter (Figure 11.6), which measures the activity of the H^+ ion electrochemically. (The construction of a pH meter is discussed in more detail in Chapter 13). Table 11.1 lists the pH values of a number of common fluids at 25°C. As you can see, the pH of body fluids varies greatly, depending on location and function. The low pH (high acidity) of gastric juices facilitates digestion whereas the higher pH of blood is necessary for the transport of oxygen.

A pOH scale analogous to the pH scale can be devised using the negative logarithm (base 10) of the hydroxide ion activity of a solution. Thus, we define pOH as

$$\text{pOH} = -\log_{10} a_{\text{OH}^-} \quad (11.6)$$

As in the case of pH, the pOH for sufficiently dilute aqueous solutions can be written as

$$\text{pOH} \approx -\log_{10} [\text{OH}^-] \quad (11.7)$$

Now consider again the ion-product constant for water at 25°C:

$$[\text{H}^+] [\text{OH}^-] = K_w = 1.01 \times 10^{-14}$$

Taking the negative logarithm of both sides, we obtain

$$\begin{aligned} -\log_{10} [\text{H}^+] - \log_{10} [\text{OH}^-] &= -\log_{10} (1.01 \times 10^{-14}) \\ &= 14.00 \end{aligned}$$

From the definitions of pH and pOH we obtain

$$\text{pH} + \text{pOH} = 14.00 \quad (11.8)$$

at 25°C. Equation 11.8 provides us with another way to express the relationship between the H^+ ion concentration and the OH^- ion concentration.

Examples 11.4 to 11.6 illustrate calculations involving pH at 25°C.

Example 11.4

The concentration of H^+ ions in a bottle of table wine was $3.2 \times 10^{-4} \text{ M}$ right after the cork was removed. Only half of the wine was consumed. The other half, after it

—Continued

Table 11.1

The pH Values of Some Common Fluids

| Sample | pH Value |
|------------------------------|-----------|
| Gastric juice in the stomach | 1.0–2.0 |
| Lemon juice | 2.4 |
| Vinegar | 3.0 |
| Grapefruit juice | 3.2 |
| Orange juice | 3.5 |
| Urine | 4.8–7.5 |
| Water exposed to air* | 5.5 |
| Saliva | 6.4–6.9 |
| Milk | 6.5 |
| Pure water | 7.0 |
| Blood | 7.35–7.45 |
| Tears | 7.4 |
| Milk of magnesia | 10.6 |
| Household ammonia | 11.5 |

*Water exposed to air for a long period of time absorbs atmospheric CO_2 to form carbonic acid, H_2CO_3 .

Continued—

had been standing open to the air for a month, was found to have a hydrogen ion concentration equal to $1.1 \times 10^{-3} M$. Calculate the pH of the wine on these two occasions.

Strategy We are given the H^+ ion concentration and asked to calculate the pH of the solution. We can use the definition of pH given in Equation 11.5—namely, $pH = -\log_{10} [H^+]$.

Solution When the bottle was first opened, $[H^+] = 3.2 \times 10^{-4} M$, so substituting this value into Equation 11.5 gives the pH:

$$\begin{aligned} pH &= -\log_{10} [H^+] \\ &= -\log_{10} (3.2 \times 10^{-4}) = 3.49 \end{aligned}$$

On the second occasion, $[H^+] = 1.1 \times 10^{-3} M$, so

$$pH = -\log_{10} (1.1 \times 10^{-3}) = 2.96$$

Comment The increase in hydrogen ion concentration (or decrease in pH) is largely the result of the conversion of some of the alcohol (ethanol) to acetic acid, a reaction that takes place in the presence of molecular oxygen.

Practice Exercise Nitric acid (HNO_3) is used in the production of fertilizer, dyes, drugs, and explosives. Calculate the pH of an HNO_3 solution having a hydrogen ion concentration of $0.76 M$.

When taking the logarithm of a quantity x , the number of significant figures in x is the same as the number of significant figures to the right of the decimal point in $\log_{10} x$. For example, $\log_{10} 1.25 \times 10^{-3} = -2.903$. Because the quantity (1.25×10^{-3}) has three significant figures, the logarithm will have three significant figures to the right of the decimal point. See Appendix 1 for further discussion of significant figures.

Example 11.5

The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. Calculate the H^+ ion concentration of the rainwater.

Strategy We are given the pH of a solution and asked to calculate $[H^+]$. Because pH is defined as $pH = -\log_{10} [H^+]$ (Equation 11.5), we can solve for $[H^+]$ by taking the antilog₁₀ of the pH; that is, $[H^+] = 10^{-pH}$.

Solution From Equation 11.5

$$pH = -\log_{10} [H^+] = 4.82$$

Therefore,

$$\log_{10} [H^+] = -4.82$$

To calculate $[H^+]$, we need to take the antilog of -4.82 :

$$[H^+] = 10^{-4.82} = 1.5 \times 10^{-5} M$$

Check Because the pH is between 4 and 5, we can expect $[H^+]$ to be between $1 \times 10^{-4} M$ and $1 \times 10^{-5} M$. Therefore, the answer is reasonable.

Practice Exercise The pH of a certain orange juice is 3.33. Calculate the H^+ ion concentration.

Example 11.6

In an NaOH solution at 25°C, $[\text{OH}^-]$ is $2.9 \times 10^{-4} M$. Calculate the pH of the solution.

Strategy Because NaOH is a strong base, it completely dissociates into ions, and so the concentration of NaOH will be equal to the OH^- concentration. Solving this problem takes two steps. First, we need to calculate pOH using Equation 11.7 ($\text{pOH} = \log_{10} [\text{OH}^-]$). Next, we use Equation 11.8 ($\text{pH} + \text{pOH} = 14.00$) to calculate the pH of the solution.

Solution According to Equation 11.7,

$$\begin{aligned}\text{pOH} &= -\log_{10} [\text{OH}^-] \\ &= -\log_{10}(2.9 \times 10^{-4}) \\ &= 3.54\end{aligned}$$

Now, to calculate the pH, we use Equation 11.8, which is valid at 25°C:

$$\begin{aligned}\text{pH} + \text{pOH} &= 14.00 \\ \text{pH} &= 14.00 - \text{pOH} \\ &= 14.00 - 3.54 = 10.46\end{aligned}$$

Alternatively, we can use the ion-product constant of water at 25°C, $K_w = [\text{H}^+][\text{OH}^-]$, to calculate $[\text{H}^+]$, and then we can calculate the pH from the $[\text{H}^+]$ using Equation 11.5. Try it.

Check The answer shows that the solution is basic ($\text{pH} > 7$), which is to be expected for an NaOH solution.

Practice Exercise The OH^- ion concentration of a blood sample at 25°C is $2.5 \times 10^{-7} M$. What is the pH of the blood?

Temperature Dependence of K_w and pH

The ion constant of water, K_w , like most equilibrium constants, depends on temperature. Recall from Section 10.4 that the temperature dependence of an equilibrium constant can be determined from the enthalpy of reaction through the van't Hoff equation (Equation 10.16). The enthalpy of reaction for the autoionization of water is +55.84 kJ mol⁻¹:



That is, the autoionization of water is an endothermic process. According to Le Châtelier's principle (Section 10.4), the equilibrium of an endothermic process will shift in the direction of products when the temperature is increased, leading to a corresponding increase in the equilibrium constant. Therefore, the value of K_w will be larger than its value at 25°C (1.01×10^{-14}) for temperatures above 25°C and smaller than its value at 25°C for temperatures below 25°C. Table 11.2 shows the value of K_w at a variety of temperatures.

At 60°C (333 K), for example, K_w is 9.61×10^{-14} , nearly 10 times larger than at 25°C. Given this value of K_w , we can calculate the H^+ ion concentration of neutral water (where $[\text{H}^+] = [\text{OH}^-]$) at 60°C as follows:

$$\begin{aligned}K_w &= [\text{H}^+][\text{OH}^-] = [\text{H}^+]^2 = 9.61 \times 10^{-14} \\ [\text{H}^+] &= 3.10 \times 10^{-7}\end{aligned}$$

Table 11.2 Temperature Dependence of the Autoionization Constant of Water (K_w) and the pH of Neutral Water

| Temperature (K) | K_w | pH of Neutral Water |
|-----------------|------------------------|---------------------|
| 273 | 1.14×10^{-15} | 7.47 |
| 298 | 1.00×10^{-14} | 7.00 |
| 313 | 2.92×10^{-14} | 6.77 |
| 333 | 9.61×10^{-14} | 6.51 |
| 373 | 5.4×10^{-13} | 6.13 |

This value is about three times larger than the corresponding value at 25°C. The pH of neutral water at this temperature is then

$$\text{pH} = -\log_{10} [\text{H}^+] = -\log_{10} (3.10 \times 10^{-7}) = 6.51$$

The values in Table 10.2 can be calculated using the van't Hoff equation (Equation 10.16) given the value of K_w at 298 K and thermodynamic data from Appendix 2.

Example 11.7

A sample of water from a hot spring at 40°C has an $[\text{H}^+]$ concentration of $2.34 \times 10^{-6} M$. What is the $[\text{OH}^-]$ concentration in this sample?

Strategy To find the $[\text{OH}^-]$ using Equation 11.3, we need to know K_w at this temperature (40°C = 313 K). According to Table 11.2, $K_w = 2.92 \times 10^{-14}$ at 313 K.

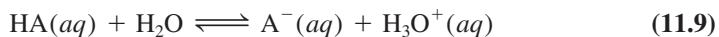
Solution From Equation 11.3, we have

$$\begin{aligned} [\text{H}^+] [\text{OH}^-] &= K_w \\ [\text{OH}^-] &= \frac{K_w}{[\text{H}^+]} \\ &= \frac{2.92 \times 10^{-14}}{2.34 \times 10^{-6}} \\ &= 1.25 \times 10^{-8} M \end{aligned}$$

Practice Exercise The pOH of an aqueous solution is 4.32 at a temperature of 60°C. Determine the pH and H^+ ion concentration of this sample.

11.3 | The Strengths of Acids and Bases Are Measured by Their Ionization Constants

Most acids are *weak acids*, which ionize only to a limited extent in water (Figure 11.7). If we represent a nonionized weak acid by HA, with conjugate base A^- , the ionization of a weak acid in aqueous solution is represented by the following equilibrium:



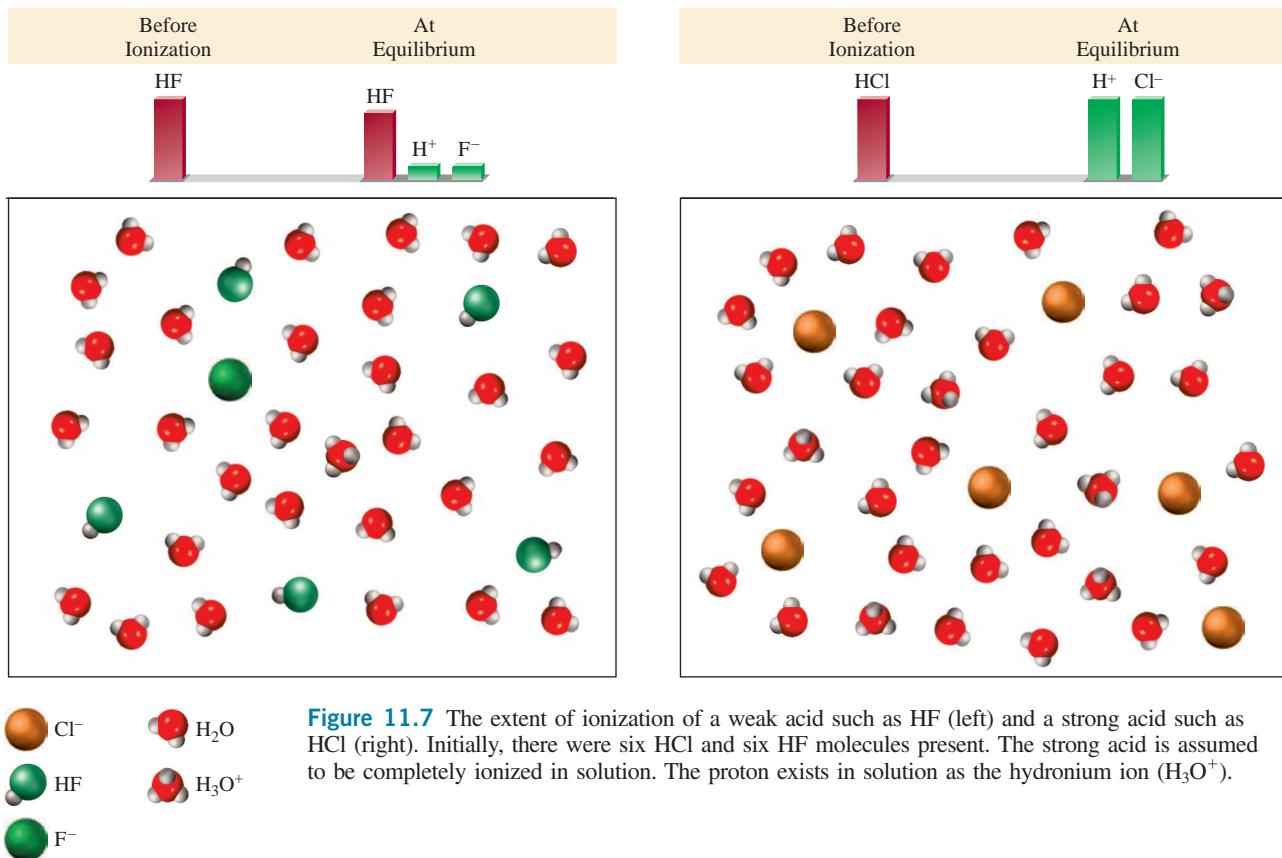


Figure 11.7 The extent of ionization of a weak acid such as HF (left) and a strong acid such as HCl (right). Initially, there were six HCl and six HF molecules present. The strong acid is assumed to be completely ionized in solution. The proton exists in solution as the hydronium ion (H_3O^+).

At equilibrium, aqueous solutions of weak acids contain a mixture of nonionized acid molecules (HA), H_3O^+ ions, and the conjugate base (A^-). Some examples of weak acids are hydrofluoric acid (HF), acetic acid (CH_3COOH), and the ammonium ion (NH_4^+).

The strength of a weak acid—that is, the extent to which it ionizes in aqueous solution—is determined by the magnitude of the equilibrium constant, called the **acid ionization constant** (K_a), of the acid ionization reaction (Equation 11.9):

$$K_a = \frac{a_{\text{H}_3\text{O}^{+}(aq)} a_{\text{A}^-(aq)}}{a_{\text{HA}(aq)} a_{\text{H}_2\text{O}(l)}} \quad (11.10)$$

where a represents the activity of each species. As with our discussion of the ion constant of water, for sufficiently dilute solutions ($<0.05 \text{ M}$), the activities of the solutes (HA , A^- , and H_3O^+) are well approximated by their concentrations (relative to the standard concentration of 1 M), and the activity of the solvent (water) can be assumed to be equal to 1, giving

$$K_a \approx \frac{[\text{H}_3\text{O}^+] [\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+] [\text{A}^-]}{[\text{HA}]} \quad (11.11)$$

For example, the K_a for the weak acid HF ($\text{HA} = \text{HF}$ and $\text{A}^- = \text{F}^-$) is given by

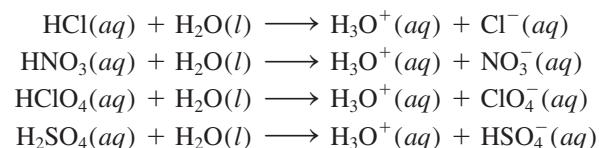
$$K_a = \frac{[\text{H}^+] [\text{F}^-]}{[\text{HF}]}$$

Table 11.3 Acid Ionization Constants of Common Weak Acids at 298 K

| Acid | K_a |
|--|-----------------------|
| HF (hydrofluoric acid) | 7.1×10^{-4} |
| HCN (hydrocyanic acid) | 4.9×10^{-10} |
| HNO ₂ (nitrous acid) | 4.5×10^{-4} |
| CH ₃ COOH (acetic acid) | 1.75×10^{-5} |
| HCOOH (formic acid) | 1.77×10^{-4} |
| ClCH ₂ COOH (chloroacetic acid) | 1.36×10^{-3} |
| CH ₃ CH(OH)COOH (lactic acid) | 1.39×10^{-4} |
| C ₆ H ₅ COOH (benzoic acid) | 6.5×10^{-5} |
| C ₆ H ₅ OH (phenol) | 1.3×10^{-10} |
| C ₉ H ₈ O ₄ (acetylsalicylic acid; aspirin) | 3.0×10^{-4} |

The larger the K_a , the stronger the acid. Table 11.3 lists the K_a values for a number of common weak acids.

As defined in Section 11.1, *strong acids* can be assumed, for practical purposes, to ionize completely in water (see Figure 11.7). There are relatively few strong acids and most are inorganic acids, such as hydrochloric acid (HCl), nitric acid (HNO₃), perchloric acid (HClO₄), and sulfuric acid (H₂SO₄):



H₂SO₄ is a diprotic acid, but we show only the first stage of ionization here because HSO₄⁻ is a weak acid. Other strong acids are hydrobromic acid (HBr) and hydroiodic acid (HI). At equilibrium, solutions of strong acids will not contain any unionized acid molecules.

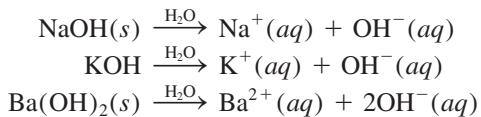
The strongest acid that can exist in aqueous solution is the hydronium ion (H₃O⁺). The K_a for the hydronium ion is the equilibrium constant for the following proton exchange reaction:



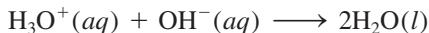
Because the species on either side of this equilibrium are the same, the equilibrium constant for this reaction is identically equal to 1, that is, the K_a for the hydronium ion is exactly 1. Acids that are stronger than the hydronium ion ($K_a > 1$) will react completely with water to yield hydronium ion and the conjugate base; therefore, they will be strong acids. This gives us a convenient definition of a strong acid as one with an acid dissociation constant greater than unity (in aqueous solution). All such acids will yield identical H₃O⁺ concentrations in water, independent of their individual K_a values—a phenomenon known as *solvent leveling*.

Like strong acids, *strong bases* are completely ionized in water (see Section 11.1). Hydroxides of alkali metals and certain alkaline earth metals are strong bases. [All alkali metal hydroxides are water soluble. Of the alkaline earth hydroxides, Be(OH)₂

and $\text{Mg}(\text{OH})_2$ are insoluble; $\text{Ca}(\text{OH})_2$ and $\text{Sr}(\text{OH})_2$ are slightly soluble; and $\text{Ba}(\text{OH})_2$ is soluble.] Some examples of strong bases are

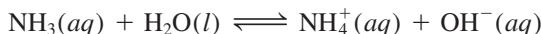


Strictly speaking, these metal hydroxides are not Brønsted bases because they cannot accept a proton. The hydroxide ion (OH^-) formed when they ionize, however, *is* a Brønsted base because it can accept a proton:



Thus, when we call NaOH or any other metal hydroxide a base, we are actually referring to the OH^- species derived from the hydroxide.

Weak bases, like weak acids, *are weak electrolytes*. Ammonia is a weak base. It ionizes to a very limited extent in water:



NH_3 does not ionize like an acid because it does not split up to form ions the way, say, HCl does. Instead, NH_3 accepts a proton from water to become the NH_4^+ ion.

The ionization of weak bases is treated in the same way as the ionization of weak bases. Consider the following reaction of a base A^- with water:



The equilibrium constant for this reaction, called the **base ionization constant** (K_b), is given by

$$K_b = \frac{a_{\text{HA}(aq)} a_{\text{OH}^-(aq)}}{a_{\text{A}^-(aq)} a_{\text{H}_2\text{O}(l)}} \approx \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} \quad (11.13)$$

where we have assumed that the solutions are sufficiently dilute so that the activities of the solutes can be approximated by their concentrations and that the activity of water is unity. For example, the K_b for NH_3 ($\text{A}^- = \text{NH}_3$ and $\text{HA} = \text{NH}_4^+$) is given by

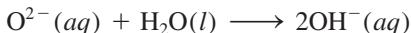
$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

The larger the K_b , the stronger the base. The K_b values for a number of common bases are listed in Table 11.4.

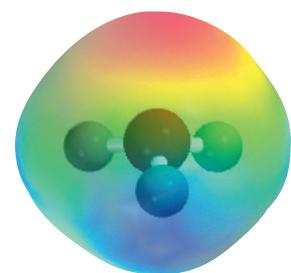
The OH^- ion is the strongest base that can exist in aqueous solution. Like the K_a for the hydronium ion, the K_b for the hydroxide ion is exactly 1 because it is the equilibrium constant for the reaction



Bases stronger than OH^- ($K_b > 1$) react with water to produce OH^- and their conjugate acids. For example, the oxide ion (O^{2-}) is a stronger base than OH^- , so it reacts with water completely as follows:



For this reason the oxide ion does not exist in aqueous solution.



The lone pair (red color) on the N atom accounts for ammonia's basicity.

Table 11.4 Base Ionization Constants (K_b) for Select Weak Bases at 298 K

| Base | K_b |
|--|-----------------------|
| $\text{C}_2\text{H}_5\text{NH}_2$ (ethylamine) | 5.6×10^{-4} |
| CH_3NH_2 (methylamine) | 4.4×10^{-4} |
| NH_3 (ammonia) | 1.8×10^{-5} |
| $\text{C}_5\text{H}_5\text{NH}_2$ (pyridine) | 1.7×10^{-9} |
| $\text{C}_6\text{H}_5\text{NH}_2$ (aniline) | 3.8×10^{-10} |
| $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2$ (caffeine) | 5.3×10^{-14} |
| $(\text{NH}_2)_2\text{CO}$ (urea) | 1.5×10^{-14} |

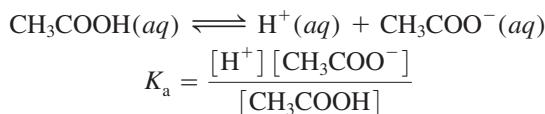
Like K_w , both the K_a for weak acids and the K_b for weak bases depend upon temperature. The temperature dependence of these quantities can be determined from the standard enthalpy change of the corresponding ionization reaction (see Equation 10.16). For example, the ΔH° for the ionization of the weak acid HF,



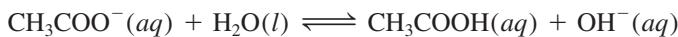
-13 kJ mol^{-1} . Thus, this reaction is exothermic. According to Le Châtelier's principle, increasing the temperature of an exothermic reaction will shift the equilibrium toward the reactants—that is, the equilibrium constant will decrease. Therefore, we expect the K_a for HF to decrease with temperature (see Problem 11.35 at the end of the chapter). As another example, consider the weak base ammonia (NH_3). The ΔH° for the ionization of NH_3 in aqueous solution is $+2.4 \text{ kJ mol}^{-1}$, indicating that this ionization is endothermic. According to Le Châtelier's principle, the K_b for NH_3 will increase with increasing temperature. This increase will be relatively weak, however, given the relatively small value of ΔH° . To determine whether a given K_a or K_b will increase or decrease with temperature, you must first determine the ΔH° for the ionization reaction. If the reaction is endothermic, then the acid or base ionization constant will increase with increasing temperature. If it is exothermic, then the ionization constant will decrease with increasing temperature.

The Relationship Between the Ionization Constants of Acids and Their Conjugate Bases

An important relationship between the acid ionization constant and the ionization constant of its conjugate base can be derived as follows, using acetic acid as an example:



The conjugate base (CH_3COO^-), supplied, for example, by a sodium acetate (CH_3COONa) solution, reacts with water according to the equation



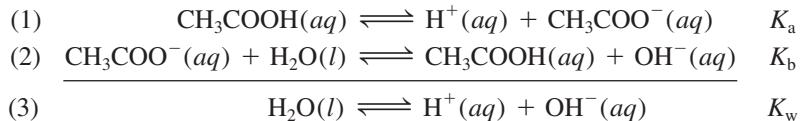
We can write the base ionization constant (Equation 11.13) as

$$K_b = \frac{[\text{CH}_3\text{COOH}] [\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

The product of these two ionization constants is given by

$$\begin{aligned} K_a K_b &= \frac{[\text{H}^+] [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \times \frac{[\text{CH}_3\text{COOH}] [\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \\ &= [\text{H}^+] [\text{OH}^-] \\ &= K_w \end{aligned}$$

This result may seem strange at first, but if we add the two chemical equations we see that the sum is simply the autoionization of water.



This example illustrates one of the rules for chemical equilibria: When two reactions are added together to give a third reaction, the equilibrium constant for the third reaction is the product of the equilibrium constants for the two added reactions (see Section 10.1). Thus, for any conjugate acid-base pair, it is always true that

$$K_a K_b = K_w \quad (11.14)$$

Expressing Equation 11.14 as

$$K_a = \frac{K_w}{K_b} \quad \text{or} \quad K_b = \frac{K_w}{K_a}$$

shows that the stronger the acid (the larger the K_a), the weaker its conjugate base (the smaller the K_b), and vice versa. This conclusion is illustrated in Example 11.8.

Example 11.8

The K_a values for hydrofluoric acid (HF) and acetic acid (CH_3COOH) at 25°C are 7.1×10^{-4} and 1.8×10^{-5} , respectively. Calculate the K_b values for their conjugate bases at this temperature.

Strategy The conjugate bases for HF and CH_3COOH are F^- and CH_3COO^- (acetate ion), respectively. The K_a 's are given, so use Equation 11.14 ($K_w = K_a K_b$) to find the K_b 's, using the value of K_w at 25°C (1.01×10^{-14}).

Solution The K_a for HF is 7.7×10^{-4} . Rearranging Equation 11.14 gives the K_b for F^- as

$$\begin{aligned} K_b &= \frac{K_w}{K_a} = \frac{1.01 \times 10^{-14}}{7.1 \times 10^{-4}} \\ &= 1.4 \times 10^{-11} \end{aligned}$$

Similarly, the K_b for the acetate ion is given by

$$\begin{aligned} K_b &= \frac{K_w}{K_a} = \frac{1.01 \times 10^{-14}}{1.8 \times 10^{-5}} \\ &= 5.6 \times 10^{-10} \end{aligned}$$

—Continued

Continued—

Check The K_b for the fluoride ion (F^-) is smaller than that for the acetate ion (CH_3COO^-), that is, F^- is a *weaker* base than CH_3COO^- . This is consistent with the fact that HF is a *stronger* acid than CH_3COOH .

Practice Exercise The values of K_b for ammonia (NH_3) and methylamine (CH_3NH_2) are 1.8×10^{-5} and 4.38×10^{-4} , respectively. Calculate the K_a values for the corresponding conjugate acids.

The values of K_a and K_b for a number of common conjugate acid-base pairs are shown in Table 11.5. Because K_a and K_b values can range over many orders of magnitude, they are often expressed on a logarithmic scale similar to pH. We define pK_a and pK_b as follows:

$$pK_a = -\log_{10} K_a \quad (11.15)$$

$$pK_b = -\log_{10} K_b \quad (11.16)$$

For example the pK_a of HF ($K_a = 7.1 \times 10^{-4}$) is $-\log_{10}(7.1 \times 10^{-4}) = 3.15$ and the pK_b of NH_3 ($K_b = 1.8 \times 10^{-5}$) is $-\log_{10}(1.8 \times 10^{-5}) = 4.74$. Taking the negative logarithm (base 10) of Equation 11.14 ($K_a K_b = K_w$) gives

$$\begin{aligned} -\log_{10} K_a K_b &= -\log_{10} K_w \\ -\log_{10} K_a - \log_{10} K_b &= -\log_{10} K_w \\ pK_a + pK_b &= -\log_{10} K_w \end{aligned} \quad (11.17)$$

Table 11.5 Relative Strengths of Select Conjugate Acid-Base Pairs

| Acid | K_a | pK_a | Conjugate Base | K_b | pK_b |
|----------------------------------|----------------------------|--------|----------------------------------|---------------------------|--------|
| HI (hydroiodic acid)* | $\sim 10^{10}$ | -10 | I^- (iodide ion) | $\sim 1 \times 10^{-24}$ | 24 |
| HBr (hydrobromic acid) | $\sim 10^9$ | -9 | Br^- (bromide ion) | $\sim 1 \times 10^{-23}$ | 23 |
| HCl (hydrochloric acid)* | $\sim 1 \times 10^6$ | -6 | Cl^- (chloride ion) | $\sim 1 \times 10^{-20}$ | 20 |
| H_2SO_4 (sulfuric acid)* | $\sim 1 \times 10^3$ | -3 | HSO_4^- (hydrogen sulfate ion) | $\sim 1 \times 10^{-17}$ | 17 |
| HNO_3 (nitric acid)* | $\sim 1 \times 10^2$ | -2 | NO_3^- (nitrate ion) | $\sim 1 \times 10^{-15}$ | 15 |
| H_3O^+ (hydronium ion) | 1 | 0.00 | H_2O (water) | 1.0×10^{-14} | 14.00 |
| HSO_4^- (hydrogen sulfate ion) | 1.3×10^{-2} | 1.89 | SO_4^{2-} (sulfate ion) | 7.7×10^{-13} | 12.11 |
| HF (hydrofluoric acid) | 7.1×10^{-4} | 3.15 | F^- (fluoride ion) | 1.4×10^{-11} | 10.85 |
| HNO_2 (nitrous acid) | 4.5×10^{-4} | 3.35 | NO_2^- (nitrite ion) | 2.2×10^{-11} | 10.65 |
| $HCOOH$ (formic acid) | 1.7×10^{-4} | 3.77 | $HCOO^-$ (formate ion) | 5.9×10^{-11} | 10.23 |
| CH_3COOH (acetic acid) | 1.8×10^{-5} | 4.74 | CH_3COO^- (acetate ion) | 5.6×10^{-10} | 9.26 |
| NH_4^+ (ammonium ion) | 5.6×10^{-10} | 9.25 | NH_3 (ammonia) | 1.8×10^{-5} | 4.75 |
| HCN (hydrocyanic acid) | 4.9×10^{-10} | 9.31 | CN^- (cyanide ion) | 2.0×10^{-5} | 4.69 |
| H_2O (water) | 1.0×10^{-14} | 14.00 | OH^- (hydroxyl ion) | 1 | 0.00 |
| NH_3 (ammonia) | $\sim 1.0 \times 10^{-34}$ | 34 | NH_2^- (amide ion) | $\sim 1.0 \times 10^{20}$ | -20 |

*The K_a for strong acids (and amide) given here are highly approximate values estimated from thermodynamic data. They are included here only to show trends in acid strength and should be used with caution.

So, at 25°C, $K_w = 1.01 \times 10^{-14}$ and

$$\text{p}K_a + \text{p}K_b = 14.00 \quad (11.18)$$

The $\text{p}K_a$ and $\text{p}K_b$ values for a number of common conjugate acid-base pairs are also given in Table 11.5.

If we know the relative strengths of two acids, we can predict the extent of reaction between one of the acids and the conjugate base of the other, as illustrated in Example 11.9.

Example 11.9

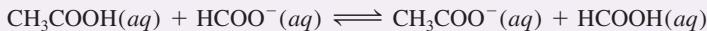
Predict whether the following reaction will favor reactants or products at equilibrium:



Strategy The problem is to determine whether, at equilibrium, the reaction will be shifted to the right, favoring HCN and NO_2^- , or to the left, favoring HNO_2 and CN^- . Which of the two (HNO_2 or HCN) is a stronger acid and hence a stronger proton donor? Which of the two (CN^- or NO_2^-) is a stronger base and hence a stronger proton acceptor? Remember that the stronger the acid, the weaker its conjugate base. The equilibrium will favor the weaker acid and the weaker conjugate base, so use Table 11.5 to compare K_a values.

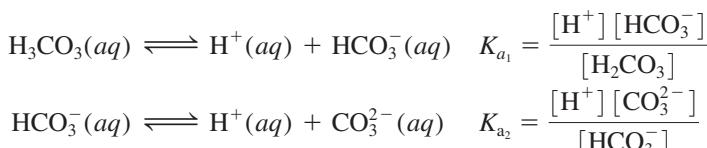
Solution According to Table 11.5, HNO_2 is a stronger acid than HCN because $K_a(\text{HNO}_2) > K_a(\text{HCN})$. Thus, CN^- is a stronger base than NO_2^- . The net reaction will proceed from left to right as written because HNO_2 is a better proton donor than HCN (and CN^- is a better proton acceptor than NO_2^-).

Practice Exercise Predict whether the equilibrium constant for the following reaction is greater than or less than 1:



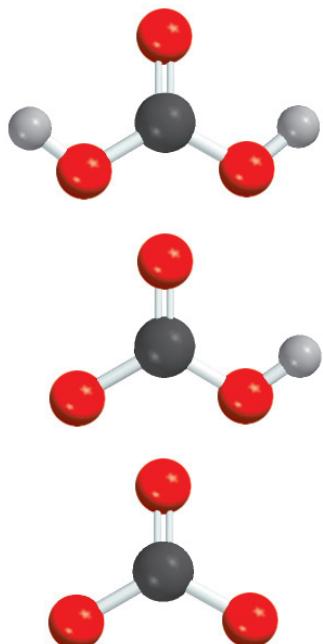
Ionization Constants for Diprotic and Triprotic Acids

The treatment of diprotic and triprotic acids is more involved than that of monoprotic acids because diprotic and triprotic acids may yield more than one hydrogen ion per molecule. Diprotic and triprotic acids ionize in a stepwise manner, that is, they lose one proton at a time. An ionization constant expression can be written for each ionization stage. Consequently, two or more equilibrium constant expressions must often be used to calculate the concentrations of species in the acid solution. For carbonic acid (H_2CO_3), for example, we write



The conjugate base in the first ionization stage becomes the acid in the second ionization stage.

Table 11.6 lists the ionization constants of several diprotic acids and one triprotic acid. For a given acid, the first ionization constant is much larger than the second ionization constant, and so on. This trend occurs because it is easier to remove an H^+ ion from a neutral molecule than to remove an additional H^+ ion from the resulting negatively charged ion.



Top to bottom: H_2CO_3 , HCO_3^- , and CO_3^{2-} .

Table 11.6 Ionization Constants of Some Diprotic Acids and a Triprotic Acid and Their Conjugate Bases at 25°C

| Name of Acid | Formula | Structure | K_a | Conjugate Base | K_b |
|--------------------------|----------------------------------|---|-----------------------|-----------------------------|-----------------------|
| Sulfuric acid | H_2SO_4 | H—O— $\begin{array}{c} \text{O} \\ \parallel \\ \text{S} \\ \parallel \\ \text{O} \end{array}$ —O—H | very large | HSO_4^- | very small |
| Hydrogen sulfate ion | HSO_4^- | H—O— $\begin{array}{c} \text{O} \\ \parallel \\ \text{S} \\ \parallel \\ \text{O} \end{array}$ —O [—] | 1.3×10^{-2} | SO_4^{2-} | 7.7×10^{-13} |
| Oxalic acid | $\text{C}_2\text{H}_2\text{O}_4$ | H—O— $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \parallel \\ \text{C} \\ \parallel \\ \text{O} \end{array}$ —O—H | 6.5×10^{-2} | C_2HO_4^- | 1.5×10^{-13} |
| Hydrogen oxalate ion | C_2HO_4^- | H—O— $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \parallel \\ \text{C} \\ \parallel \\ \text{O} \end{array}$ —O [—] | 6.1×10^{-5} | $\text{C}_2\text{O}_4^{2-}$ | 1.6×10^{-10} |
| Sulfurous acid* | H_2SO_3 | H—O— $\begin{array}{c} \text{O} \\ \parallel \\ \text{S} \\ \parallel \\ \text{O} \end{array}$ —O—H | 1.3×10^{-2} | HSO_3^- | 7.7×10^{-13} |
| Hydrogen sulfite ion | HSO_3^- | H—O— $\begin{array}{c} \text{O} \\ \parallel \\ \text{S} \\ \parallel \\ \text{O} \end{array}$ —O [—] | 6.3×10^{-8} | SO_3^{2-} | 1.6×10^{-7} |
| Carbonic acid | H_2CO_3 | H—O— $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \parallel \\ \text{O} \end{array}$ —O—H | 4.2×10^{-7} | HCO_3^- | 2.4×10^{-8} |
| Hydrogen carbonate ion | HCO_3^- | H—O— $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \parallel \\ \text{O} \end{array}$ —O [—] | 4.8×10^{-11} | CO_3^{2-} | 2.1×10^{-4} |
| Hydrosulfuric acid | H_2S | H—S—H | 9.5×10^{-8} | HS^- | 1.1×10^{-7} |
| Hydrogen sulfide ion† | HS^- | H—S [—] | 1×10^{-19} | S^{2-} | 1×10^5 |
| Phosphoric acid | H_3PO_4 | H—O— $\begin{array}{c} \text{O} \\ \parallel \\ \text{P} \\ \\ \text{O} \\ \\ \text{H} \end{array}$ —O—H | 7.5×10^{-3} | H_2PO_4^- | 1.3×10^{-12} |
| Dihydrogen phosphate ion | H_2PO_4^- | H—O— $\begin{array}{c} \text{O} \\ \parallel \\ \text{P} \\ \\ \text{O} \\ \\ \text{H} \end{array}$ —O [—] | 6.2×10^{-8} | HPO_4^{2-} | 1.6×10^{-7} |
| Hydrogen phosphate ion | HPO_4^{2-} | H—O— $\begin{array}{c} \text{O} \\ \parallel \\ \text{P} \\ \\ \text{O} \\ \\ \text{O} \end{array}$ —O [—] | 4.8×10^{-13} | PO_4^{3-} | 2.1×10^{-2} |

* H_2SO_3 has never been isolated and exists in only minute concentration in aqueous solution of SO_2 . The K_a value here refers to the process $\text{SO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{HSO}_3^-(aq)$.

†The ionization constant of HS^- is very low and difficult to measure. The value listed here is only an estimate.

11.4 | The pH of an Acid or Base Can Be Calculated If Its Ionization Constant Is Known

Strong Acids and Bases

Calculating the pH of solutions of strong monoprotic acids or strong bases is straightforward because they can be assumed to ionize completely in water. Therefore, the concentration of H_3O^+ (in the case of strong monoprotic acids) or OH^- (in the case of strong bases) will be equal to the initial concentration of acid or base, respectively, as long as the solution is sufficiently concentrated that the contribution from the autoionization of water is negligible.

Example 11.10 shows how to calculate the pH of a solution containing a strong monoprotic acid and a solution containing a strong base.

Example 11.10

Calculate the pH of (a) a $1.7 \times 10^{-4} M$ HCl solution and (b) a $2.3 \times 10^{-3} M$ $\text{Ba}(\text{OH})_2$ solution.

Strategy HCl is a strong acid and $\text{Ba}(\text{OH})_2$ is a strong base, so these species are completely ionized [no HCl or $\text{Ba}(\text{OH})_2$ will remain] in aqueous solution. Once the $[\text{H}^+]$ is known in part (a), we can use Equation 11.5 ($\text{pH} = -\log_{10} [\text{H}^+]$) to calculate pH. Once $[\text{OH}^-]$ is known in part (b), we can use Equation 11.7 ($\text{pOH} = -\log_{10} [\text{OH}^-]$) to calculate pOH, and then Equation 11.8 ($\text{pH} + \text{pOH} = 14.00$) to calculate pH.

Solution (a) The ionization of HCl is



HCl is a strong monoprotic acid so dissociation is complete; therefore, the concentration of H^+ and Cl^- ions is the same as the initial HCl concentration:

$$[\text{H}^+] = [\text{Cl}^-] = [\text{HCl}]_0 = 1.7 \times 10^{-4} M$$

Thus,

$$\begin{aligned}\text{pH} &= -\log_{10} [\text{H}^+] = -\log_{10} (1.7 \times 10^{-4}) \\ &= 3.77\end{aligned}$$

(b) $\text{Ba}(\text{OH})_2$ is a strong base, and each $\text{Ba}(\text{OH})_2$ unit produces two OH^- ions:



Therefore, the concentration of OH^- ions in the solution will be twice the initial concentration of $\text{Ba}(\text{OH})_2$:

$$\begin{aligned}[\text{OH}^-] &= 2 \times [\text{Ba}(\text{OH})_2] = 2 \times (2.3 \times 10^{-3} M) \\ &= 4.6 \times 10^{-3} M\end{aligned}$$

Thus,

$$\begin{aligned}\text{pOH} &= -\log_{10} [\text{OH}^-] = -\log_{10} [4.6 \times 10^{-3}] \\ &= 2.34\end{aligned}$$

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Continued—

and from Equation 11.8,

$$\begin{aligned}\text{pH} &= 14.00 - \text{pOH} \\ &= 14.00 - 2.34 \\ &= 11.66\end{aligned}$$

Comment In both parts (a) and (b), we have neglected the contribution of the autoionization of water to $[\text{H}^+]$ and $[\text{OH}^-]$ because $1.0 \times 10^{-7} M$ is so small compared with $1.7 \times 10^{-4} M$ and $4.6 \times 10^{-3} M$. Also, the calculated pH values may differ slightly from the actual values due to the nonideality of the solution. This will be most pronounced in the $\text{Ba}(\text{OH})_2$ solution because it is less dilute and because a Ba^{2+} ion is highly charged and will interact strongly with other ions in the solution.

Practice Exercise Calculate the pH of a $1.8 \times 10^{-5} M$ $\text{Ba}(\text{OH})_2$ solution.

If the strong acid or strong base is very dilute ($< 10^{-6} M$), then it is necessary to take into account the autoionization of water. This case is discussed later in this section.

Weak Monoprotic Acids

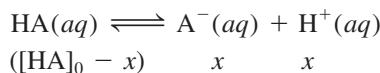
To calculate the pH of a weak monoprotic acid, it is necessary to take into account the ionization equilibrium



where the acid and conjugate base are represented by HA and A^- , respectively. Ignoring the autoionization of water, the concentrations of HA, A^- , and H_3O^+ are related by the equilibrium constant expression (Equation 11.11):

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (11.11)$$

If we let $[\text{HA}]_0$ be the initial concentration of the acid and x be the concentrations of $[\text{A}^-]$ and $[\text{H}_3\text{O}^+]$ at equilibrium, then we have from the stoichiometry,



The equilibrium constant expression becomes

$$\begin{aligned}K_a &= \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(x)(x)}{[\text{HA}]_0 - x} \\ K_a &= \frac{x^2}{[\text{HA}]_0 - x}\end{aligned} \quad (11.19)$$

which gives the following equation for $x = [\text{H}_3\text{O}^+]$:

$$x^2 + K_a x - K_a[\text{HA}]_0 = 0 \quad (11.20)$$

Equation 11.20 is a quadratic equation of the form $ax^2 + bx + c = 0$, for which the general solution is given by the quadratic formula:

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

If K_a is sufficiently small or $[HA]_0$ is sufficiently large, then the amount of acid dissociated, x , will be small compared to $[HA]_0$ and the x in the denominator of Equation 11.19 can be neglected to give

$$x \approx \sqrt{K_a[HA]_0} \quad (11.21)$$

This approximation is generally considered valid as long as the value of x is less than 5 percent of $[HA]_0$ because 5 percent is typically the level of accuracy to which K_a is known. If this approximation is used, though, it is necessary to confirm that the resulting value of x is indeed less than 5 percent of $[HA]_0$.

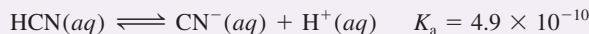
Once $x = [H^+]$ is calculated, the pH can be found from Equation 11.5. Example 11.11 shows how to calculate the pH for a weak acid solution.

Example 11.11

Calculate the pH of (a) a 0.50 M HCN solution and (b) a 0.050 M HF solution.

Strategy To determine the pH of these weak acids, it is necessary to know their K_a values. According to Table 11.3, $K_a = 4.9 \times 10^{-10}$ for HCN and 7.1×10^{-4} for HF. Use the procedure outlined previously (which utilizes Equations 11.19 and 11.21) to determine pH.

Solution (a) The ionization of HCN is given by



If we let $x = [\text{H}^+] = [\text{CN}^-]$, then Equation 11.19 gives (with $[\text{HCN}]_0 = 0.50 \text{ M}$)

$$K_a = 4.9 \times 10^{-10} = \frac{x^2}{0.05 - x}$$

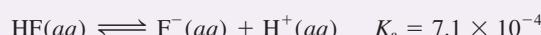
The magnitude of K_a is very small relative to $[\text{HCN}]_0$, so we can ignore the x in the denominator and use Equation 11.21 to give

$$\begin{aligned} x &\approx \sqrt{K_a[\text{HA}]_0} = \sqrt{(4.9 \times 10^{-10})(0.50)} \\ &= 1.6 \times 10^{-5} \text{ M} \end{aligned}$$

The value of x is well below 5 percent of $[\text{HCN}]_0 = 0.50 \text{ M}$, so the approximation is justified. The pH of the solution can then be calculated from Equation 11.5:

$$\begin{aligned} \text{pH} &= -\log_{10} [\text{H}_3\text{O}^+] = -\log_{10} x \\ &= 4.80 \end{aligned}$$

(b) The ionization of HF is given by



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If we let $x = [\text{H}_3\text{O}^+] = [\text{F}^-]$, then Equation 11.19 gives (with $[\text{HF}]_0 = 0.050 \text{ M}$)

$$K_a = 7.1 \times 10^{-4} = \frac{x^2}{0.050 - x}$$

If we assume that x is small relative to $[\text{HF}]_0$, we obtain

$$\begin{aligned} x &\approx \sqrt{K_a[\text{HA}]_0} = \sqrt{(7.1 \times 10^{-4})(0.050)} \\ &= 5.9 \times 10^{-3} \text{ M} \end{aligned}$$

This value of x is greater than 5 percent of 0.050 M, so the approximation is not valid and we cannot ignore x in the denominator of the equilibrium constant expression. Starting from the ionization equilibrium expression for HF,

$$7.1 \times 10^{-4} = \frac{x^2}{0.050 - x}$$

we get

$$x^2 + (7.1 \times 10^{-4})x - 3.6 \times 10^{-5} = 0$$

The quadratic formula gives

$$\begin{aligned} x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-7.1 \times 10^{-4} \pm \sqrt{(7.1 \times 10^{-4})^2 - 4(1)(-3.6 \times 10^{-5})}}{2(1)} \\ &= \frac{-7.1 \times 10^{-4} \pm 0.012}{2} \\ &= 5.6 \times 10^{-3} \text{ M} \quad \text{or} \quad -6.4 \times 10^{-3} \text{ M} \end{aligned}$$

The second solution ($-6.4 \times 10^{-3} \text{ M}$) is physically impossible because the concentration of ions produced as a result of ionization cannot be negative. Choosing $x = 5.6 \times 10^{-3} \text{ M}$, gives a pH of

$$\text{pH} = -\log_{10}(5.6 \times 10^{-3}) = 2.25$$

Practice Exercise Calculate the pH of (a) a 0.00100 M solution of nitrous acid (HNO_2), and (b) a 0.0153 M solution of formic acid (HCOOH).

Percent Ionization

The magnitude of K_a indicates the strength of an acid (as K_a increases, so does the strength of the acid). Another measure of the strength of an acid is its **percent ionization**, which is defined as

$$\text{percent ionization} = \frac{\text{ionized acid concentration at equilibrium}}{\text{initial concentration of acid}} \times 100\% \quad (11.22)$$

We can compare the strengths of acids in terms of percent ionization only if the concentrations of the acids are the same.

The stronger the acid, the greater the percent ionization. For a monoprotic acid HA, the concentration of the acid that undergoes ionization is equal to the concentration

of the H^+ ions or the concentration of the A^- ions at equilibrium. Therefore, we can write the percent ionization as

$$\text{percent ionization} = \frac{[\text{H}^+]}{[\text{HA}]_0} \times 100\%$$

where $[\text{H}^+]$ is the H^+ concentration at equilibrium and $[\text{HA}]_0$ is the initial concentration of weak acid HA.

Using the solution to Example 11.11(b), where $[\text{H}^+] = 5.6 \times 10^{-3} M$, the percent ionization of a $0.050 M$ HF solution is

$$\text{percent ionization} = \frac{5.6 \times 10^{-3} M}{0.050 M} \times 100\% = 11\%$$

Thus, only about one out of every 9 HF molecules has ionized. This should be expected, though, because HF is a weak acid.

The extent to which a weak acid ionizes depends on the initial concentration of the acid. The more dilute the solution, the greater the percent ionization (Figure 11.8). In qualitative terms, when an acid is diluted, the number of particles (nonionized acid molecules plus ions) per unit volume is reduced. According to Le Châtelier's principle (see Section 10.4), to counteract this "stress" (that is, the dilution), the equilibrium shifts from nonionized acid to H^+ and its conjugate base to produce more particles (ions).

The dependence of percent ionization on initial concentration can be illustrated by the $0.050 M$ HF solution from Example 11.11(b), where the equilibrium concentration was found to be $5.6 \times 10^{-3} M$. We have just shown that the percent ionization of this solution is 11 percent. If we repeat the calculation in Example 11.11(b) for a concentration of $0.50 M$, we obtain an equilibrium concentration of $0.019 M$, which gives a percent ionization of

$$\frac{0.019 M}{0.050 M} \times 100\% = 3.8\%$$

Thus, a more dilute HF solution has a greater percent ionization of the acid.

Weak Base Solutions

The calculation of the pH of weak base solutions is similar to the method outlined previously (see Example 11.11) for calculating the pH of weak acids. The determination of pH for a weak base is outlined in Example 11.12.

Example 11.12

Determine the pH of an ammonia solution that is (a) $0.40 M$ and (b) $0.004 M$.

Strategy The procedure here is similar to the one used for a weak acid (see Example 11.11). For the ionization of ammonia, the major species in solution at equilibrium are NH_3 , NH_4^+ , and OH^- . The hydrogen ion concentration is very small as expected for a basic solution, so it will only be a minor species in solution. As in the case of weak acids, we can usually ignore contributions from the autoionization of water, unless the solution is very dilute.

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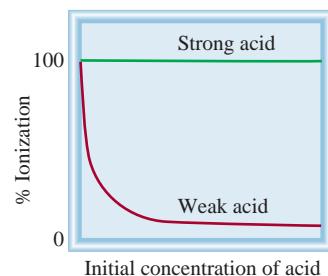


Figure 11.8 Dependence of percent ionization on the initial concentration of acid. Note that at very low concentrations, all acids (weak and strong) are almost completely ionized.

Continued—

Solution The ionization reaction is



At equilibrium the concentrations of the various solutes are related by

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

If we ignore the $[\text{OH}^-]$ contribution from the autoionization of water, the $[\text{NH}_4^+]$ and $[\text{OH}^-]$ will be equal, given the stoichiometry of the NH_3 ionization reaction. If we let x be the equilibrium concentration of NH_4^+ and OH^- in mol L⁻¹, we can summarize as follows:

| | $[\text{NH}_3]$ | $[\text{NH}_4^+]$ | $[\text{OH}^-]$ |
|-----------------|-----------------------|-------------------|-----------------|
| Initial (M) | $[\text{NH}_3]_0$ | 0.00 | 0.00 |
| Change (M) | $-x$ | $+x$ | $+x$ |
| Equilibrium (M) | $[\text{NH}_3]_0 - x$ | x | x |

Using these concentrations, the expression for K_b becomes

$$K_b = \frac{x^2}{[\text{NH}_3]_0 - x}$$

If we apply the approximation $[\text{NH}_3]_0 - x \approx [\text{NH}_3]_0$, assuming that x is small, we get

$$\begin{aligned} x^2 &\approx K_b[\text{NH}_3]_0 \\ x &= \sqrt{K_b[\text{NH}_3]_0} \end{aligned}$$

Otherwise, we have the following quadratic equation:

$$x^2 + K_b x - [\text{NH}_3]_0 K_b = 0$$

(a) Here $[\text{NH}_3]_0 = 0.40 \text{ M}$. If we assume that x is small, then

$$\begin{aligned} x &= \sqrt{K_b[\text{NH}_3]_0} = \sqrt{(1.8 \times 10^{-5})(0.40)} \\ &= 2.7 \times 10^{-3} \text{ M} \end{aligned}$$

To test the approximation, we write

$$\frac{2.7 \times 10^{-3} \text{ M}}{0.40 \text{ M}} \times 100\% = 0.68\%$$

The approximation is valid, therefore, because this value is less than 5 percent.

The pH of the solution can be calculated by first calculating its pOH. For a sufficiently dilute solution

$$\begin{aligned} \text{pOH} &= -\log_{10} [\text{OH}^-] = -\log_{10} x \\ &= -\log_{10} (2.7 \times 10^{-3}) \\ &= 2.57 \end{aligned}$$

The pH at 25°C is then given by

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.57 = 11.43$$

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(b) Here $[\text{NH}_3]_0 = 0.0040 \text{ M}$. If we assume that x is small, then

$$\begin{aligned} x &= \sqrt{K_a [\text{NH}_3]_0} = \sqrt{(1.8 \times 10^{-5})(0.0040)} \\ &= 2.7 \times 10^{-4} \text{ M} \end{aligned}$$

To test the approximation, we write

$$\frac{2.7 \times 10^{-4} \text{ M}}{0.0040 \text{ M}} \times 100\% = 6.8\%$$

This is larger than 5 percent, so the approximation is invalid and we must use the quadratic equation:

$$\begin{aligned} x^2 + K_b x - [\text{NH}_3]_0 K_b &= 0 \\ x^2 + (1.8 \times 10^{-5}) x - (7.2 \times 10^{-8}) &= 0 \end{aligned}$$

The quadratic formula then gives

$$\begin{aligned} x &= \frac{-1.8 \times 10^{-5} \pm \sqrt{(1.8 \times 10^{-5})^2 - 4(1)(-7.2 \times 10^{-8})}}{2} \\ &= -2.8 \times 10^{-4} \text{ M} \text{ or } 2.6 \times 10^{-4} \text{ M} \end{aligned}$$

The first solution is physically impossible because concentrations must be positive, so

$$x = 2.6 \times 10^{-4} \text{ M}$$

Proceeding as in part (a),

$$\begin{aligned} \text{pOH} &= -\log_{10} [\text{OH}^-] = -\log_{10} x \\ &= -\log_{10} (2.6 \times 10^{-4}) \\ &= 3.60 \end{aligned}$$

The pH at 25°C is then given by

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.60 = 10.40$$

Comment As with weak acids, the percent ionization of NH_3 (and weak bases, in general) in aqueous solution increases with decreasing concentration.

Practice Exercise Calculate the pH of a methylamine solution with an initial concentration of (a) 0.26 M and (b) 0.0026 M.

The pH of Dilute Acid and Base Solutions

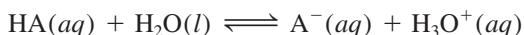
In the previous calculations, we have assumed that the autoionization of water made a negligible contribution to the OH^- and H_3O^+ concentrations, relative to the contribution from the added acid or base. This is true as long as the solution of acid or base is not very dilute. To see this, consider a $1.0 \times 10^{-8} \text{ M}$ in HCl solution at 25°C. Ignoring the autoionization of water, we would calculate the pH assuming that all the $[\text{H}_3\text{O}^+]$ in solution comes from the complete ionization of the strong acid HCl:

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+] = -\log_{10} (1.0 \times 10^{-8}) = 8.00$$

Thus, we would calculate that this solution would be basic ($\text{pH} > 7$) at 25°C , which makes no sense physically—you cannot make a basic solution by adding a small amount of acid to neutral water.

Dilute Solutions of Weak Acids

Consider, for example, the ionization of a weak acid in aqueous solution:



For nondilute solutions, we assumed that the contribution to the H_3O^+ concentration from the autoionization of water was negligible, allowing us to equate $[\text{H}_3\text{O}^+]$ and $[\text{A}^-]$. However, because the autoionization of water also contributes H_3O^+ ions, this equality is no longer true if the autoionization of water cannot be ignored. Therefore, in addition to the expression for K_a (Equation 11.11),

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

the equilibrium expression for the autoionization of water (Equation 11.3) must also be satisfied:

$$K_w = [\text{H}^+][\text{OH}^-]$$

These two equations contain four concentration variables ($[\text{H}^+]$, $[\text{OH}^-]$, $[\text{HA}]$, and $[\text{A}^-]$), so two additional equations are necessary to completely specify this system. One additional equation arises from the fact that the total amount of “A” is conserved (mass balance), so

$$[\text{HA}] + [\text{A}^-] = [\text{HA}]_0 \quad (11.23)$$

where $[\text{HA}]_0$ is the initial concentration of HA before dissociation. Also, the solution must be electrically neutral, that is, the ion concentrations must be such that the total number of positive charges equals the total number of negative charges. This condition (charge balance) requires that

$$[\text{OH}^-] + [\text{A}^-] = [\text{H}^+] \quad (11.24)$$

If we let $x = [\text{H}^+]$, these four simultaneous equations (Equation 11.3, 11.11, 11.23, and 11.24) can be solved (see Problem 11.102) to give a cubic equation for $x = [\text{H}^+]$:

$$x^3 + K_a x^2 - (K_w + K_a [\text{HA}]_0) x - K_a K_w = 0 \quad (11.25)$$

Equation 11.25 must be used if the acid is very dilute, very weak, or both, such that the H^+ ion concentration is expected to be less than $10^{-6} M$. (If K_w can be assumed to be negligible, Equation 11.25 reduces to Equation 11.20, as expected.) Although there is no simple formula for the roots of a cubic equation, Equation 11.25 can be solved using a graphing calculator or a computer program such as Mathematica or Mathcad, as illustrated in Example 11.13.

Example 11.13

Calculate the pH of a $2.0 \times 10^{-7} M$ acetic acid (CH_3COOH) solution at 25°C .

Strategy The solution is very dilute with an initial concentration of acetic acid that is very close to the H^+ concentration of neutral water, so the autoionization of water

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cannot be neglected when determining the pH. Therefore, we must use Equation 11.25 to determine the H^+ ion concentration. K_a for acetic acid is 1.8×10^{-5} .

Solution Using $[\text{HA}]_0 = 2.0 \times 10^{-7} M$, $K_a = 1.8 \times 10^{-5}$, and $K_w = 1.0 \times 10^{-14}$, Equation 11.25 gives

$$\begin{aligned}x^3 + K_a x^2 - (K_w + K_a [\text{HA}]_0) x - K_a K_w &= 0 \\x^3 + (1.8 \times 10^{-5}) x^2 - (3.6 \times 10^{-12}) x - (1.8 \times 10^{-19}) &= 0\end{aligned}$$

The coefficients of this equation are too small to be accurately solved using standard graphing calculator or computer software, so it is useful to recast the equation by transforming to a new variable $z = 10^7 x$. (Because we expect the value of x to be between 10^{-6} and 10^{-7} , z should be a number between 1 and 10.) Applying this transformation and dividing both sides of the equation by 10^{-21} gives

$$z^3 + 180z^2 - 360z - 180 = 0$$

Using a graphing calculator (or appropriate computer program), we find the solutions (roots) of this cubic polynomial equation are -182 , -0.414 , and 2.310 . The first two solutions are negative, so they are physically impossible. Therefore, the H^+ ion concentration is $2.3 \times 10^{-7} M$, after converting back to x from z . This value gives a pH of $-\log_{10}(2.3 \times 10^{-7}) = 6.64$.

Comment The acetic acid could only contribute, at a maximum, an H^+ concentration of $2.0 \times 10^{-7} M$ (the initial concentration of CH_3COOH) to this solution. The fact that the calculated $[\text{H}^+]$ is larger than $2.0 \times 10^{-7} M$ indicates that the autoionization of water is nonnegligible in this case.

Practice Exercise Calculate the pH of a $1.0 \times 10^{-4} M$ solution of HCN ($K_a = 4.9 \times 10^{-10}$).

Very Dilute Solutions of Strong Acids

Equation 11.25 can be simplified somewhat in the case of dilute strong acids. For a strong acid, the value of K_a is large and only the terms containing K_a in Equation 11.25 are significant. In this strong acid limit, Equation 11.25 becomes

$$x^2 - [\text{HA}]_0 x - K_w = 0 \quad (11.26)$$

(If K_w is neglected, we get $x = [\text{H}^+] = [\text{HA}]_0$, which is the usual equation for the H^+ ion concentration of a strong acid.)

Example 11.14 shows how to use Equation 11.26 to determine the pH of a very dilute strong acid.

Example 11.14

Calculate the pH of a $1.0 \times 10^{-7} M$ solution of HCl.

Strategy The initial concentration of HCl is less than $10^{-6} M$; therefore, the autoionization of water cannot be ignored. Because this is a strong acid, we can use Equation 11.26 to calculate the pH.

Solution Using the initial concentration of HCl given, Equation 11.26 gives

$$x^2 - (1.0 \times 10^{-7}) x - (1.0 \times 10^{-14}) = 0$$

—Continued

Continued—

This is a quadratic equation, so the solution can be determined using the quadratic formula:

$$x = \frac{1.0 \times 10^{-7} \pm \sqrt{(1.0 \times 10^{-7})^2 - 4(1)(-1.0 \times 10^{-14})}}{2}$$

$$= 1.6 \times 10^{-7} M \quad \text{or} \quad -6.2 \times 10^{-8} M$$

The second solution is physically impossible, so $x = [H^+] = 1.6 \times 10^{-7} M$, which gives a pH of 6.80.

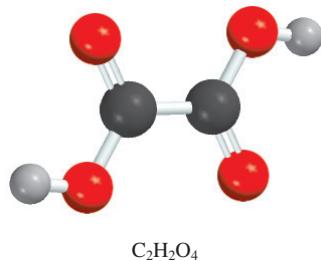
Practice Exercise Calculate the pH of a $5.0 \times 10^{-8} M$ solution of nitric acid (HNO_3).

Dilute Solutions of Bases

The pH of dilute solutions of weak and strong bases for which the autoionization of water cannot be ignored can be determined by the same procedures used to derive Equations 11.25 and 11.26 for acids. The corresponding equations for dilute weak and strong bases are identical to Equations 11.25 and 11.26, except that K_a is replaced with K_b and x represents $[OH^-]$.

The pH of Diprotic and Triprotic Acids

Example 11.15 shows how to calculate the pH of diprotic acid by calculating the equilibrium concentrations of all the species present in aqueous solution.



Example 11.15

Oxalic acid ($C_2H_2O_4$) is a poisonous substance used chiefly as a bleaching and cleansing agent (for example, to remove bathtub rings). Calculate the concentrations of all the species present at equilibrium in a $0.10 M$ solution of oxalic acid.

Strategy Determining the equilibrium concentrations of the species of a diprotic acid in aqueous solution is more involved than for a monoprotic acid. Follow the same procedure as that used for a monoprotic acid for each stage, as in Example 11.11. Remember that the conjugate base from the first stage of ionization becomes the acid for the second stage of ionization.

Solution We proceed as follows:

First ionization stage: The first ionization of oxalic acid is given by



Letting x be the equilibrium concentration of H^+ and $C_2HO_4^-$, Equation 11.19 gives

$$K_{a_1} = \frac{x^2}{[C_2HO_4]_0 - x}$$

$$6.5 \times 10^{-2} = \frac{x^2}{0.10 - x}$$

If we ignore the x in the denominator (assuming it is small relative to 0.10), we obtain

$$x = 0.081 M$$

—Continued

Continued—

This concentration is larger than 5 percent of the initial concentration, so we must recalculate x using the quadratic equation:

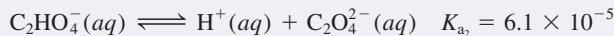
$$x^2 + (6.5 \times 10^{-2})x - 6.5 \times 10^{-3} = 0$$

The result is $x = 0.054\text{ M}$.

The second ionization constant is significantly smaller than the first (6.1×10^{-5} versus 6.5×10^{-2}), so the second ionization will make very little additional contribution to the H^+ ion concentration. Therefore, we can calculate the pH of the solution at this point:

$$\text{pH} = -\log_{10}(0.054) = 1.27$$

Second ionization stage: The second ionization of oxalic acid is given by



Letting y be the equilibrium concentration of H^+ and $\text{C}_2\text{O}_4^{2-}$ ions in mol L^{-1} , we construct the following table:

| | C_2HO_4^- | H^+ | $\text{C}_2\text{O}_4^{2-}$ |
|---------------------|---------------------------|--------------|-----------------------------|
| Initial (M) | 0.054 | 0.054 | 0 |
| Change (M) | $-y$ | $+y$ | $+y$ |
| Equilibrium (M) | $0.054 - y$ | $0.054 + y$ | y |

Thus, the equilibrium expression for the second ionization stage becomes

$$K_{a_2} = \frac{[\text{H}^+][\text{C}_2\text{O}_4^{2-}]}{[\text{C}_2\text{HO}_4^-]}$$

$$6.1 \times 10^{-5} = \frac{(0.054 + y)(y)}{0.054 - y}$$

Applying the approximation $0.054 + y \approx 0.054$ and $0.054 - y \approx 0.054$, we obtain

$$6.1 \times 10^{-5} = \frac{(0.054)(y)}{0.054}$$

$$y = 6.1 \times 10^{-5}\text{ M}$$

This value is less than 5 percent of 0.054, so the approximation is justified.

Summary:

$$[\text{H}^+] = [\text{C}_2\text{HO}_4^-] = 0.054\text{ M}$$

$$[\text{C}_2\text{H}_2\text{O}_4] = 0.10\text{ M} - 0.054\text{ M} = 0.046\text{ M}$$

$$[\text{C}_2\text{O}_4^{2-}] = 6.1 \times 10^{-5}$$

$$[\text{OH}^-] = K_w/[\text{H}^+] = 1.0 \times 10^{-14}/0.054 = 1.9 \times 10^{-13}\text{ M}$$

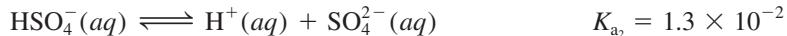
Practice Exercise Calculate the concentrations of all species present in a 0.01 M solution of oxalic acid.

Example 11.15 shows that for diprotic acids, if $K_{a_1} \gg K_{a_2}$, then we can assume that the concentration of H^+ ions is the product of only the first stage of ionization. Furthermore, the concentration of the conjugate base for the second stage of ionization

is numerically equal to K_{a_2} . One important exception to this is sulfuric acid (H_2SO_4). The first ionization,

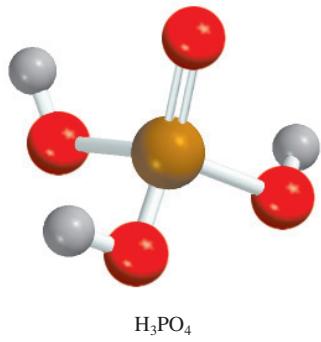
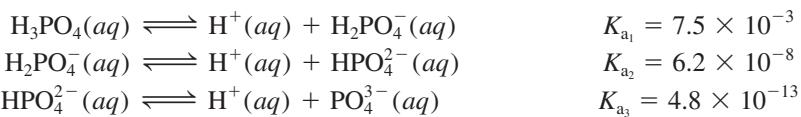


is complete (sulfuric acid is a strong acid). In addition, the second ionization,



has a large enough K_a that it makes a nonnegligible contribution to the H^+ ion concentration.

The procedure for calculating the pH of a triprotic acid is similar to that for a diprotic acid. In this case of a triprotic acid, both the second and third ionizations do not generally affect the pH. For example, phosphoric acid (H_3PO_4) is a triprotic acid (i.e., it has three ionizable hydrogen atoms):

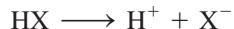


Phosphoric acid is a weak acid, though, and its ionization constants decrease markedly for the second and third stages. Thus, in a solution containing phosphoric acid, the concentration of the nonionized acid is the highest, and the only other species present in significant concentrations are H^+ and H_2PO_4^- ions.

11.5 | The Strength of an Acid Is Determined in Part by Molecular Structure

The strength of an acid depends on a number of factors, such as the properties of the solvent, the temperature, and the molecular structure of the acid. When we compare the strengths of two acids, we can eliminate some variables by considering their properties in the same solvent and at the same temperature and concentration. Then we can focus on the structure of the acids.

Consider a certain acid HX. The strength of HX is measured by its tendency to ionize in solution:



Two factors influence the extent to which the acid ionizes. One is the strength of the H—X bond. The stronger the bond, the more difficult it is for the HX molecule to break up and hence the *weaker* the acid. The other factor is the polarity of the H—X bond. Any difference in the electronegativities between H and X results in a polar bond:



If the bond is highly polarized (that is, if there is a large accumulation of positive and negative charges on H and X^-), HX will tend to break up into H^+ and X^- ions. Thus, a high degree of polarity characterizes a *stronger* acid. In the following sections, we consider some examples in which either bond strength or bond polarity plays a prominent role in determining acid strength.

Table 11.7 Bond Enthalpy and Acid Strengths for Hydrohalic Acids

| Acid | Bond Enthalpy (kJ mol ⁻¹) | K_a | Acid Strength |
|------|---------------------------------------|----------------------|---------------|
| HF | 568.2 | 7.1×10^{-4} | weak |
| HCl | 431.9 | $\sim 10^7$ | strong |
| HBr | 366.1 | $\sim 10^9$ | strong |
| HI | 298.3 | $\sim 10^{10}$ | strong |

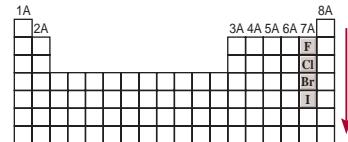
Hydrohalic Acids

The halogens form a series of binary acids called the hydrohalic acids (HF, HCl, HBr, and HI). Of this series, which factor (bond strength or bond polarity) is predominant in determining the strength of the binary acids? Consider first the strength of the H—X bond in each of these acids. According to Table 11.7, HF has the highest bond enthalpy of the four hydrogen halides and HI has the lowest. It takes 568.2 kJ mol⁻¹ to break the H—F bond and only 298.3 kJ mol⁻¹ to break the H—I bond. Based on bond energy, HI should be the strongest acid because it has the easiest bond to break to form the H⁺ and I⁻ ions. Next, consider the polarity of the H—X bond. In this series of four acids, the polarity of the bond decreases from HF to HI because F is the most electronegative of the halogens (see Figure 3.9). Based on bond polarity, then, HF should be the strongest acid because it has the largest accumulation of positive and negative charges on the H and F atoms, respectively. Thus, we have two competing factors to consider when determining the strength of binary acids. The fact that HI is a strong acid and HF is a weak acid indicates that bond energy is the predominant factor in determining the acid strength of binary acids. In this series of binary acids, the weaker the bond, the stronger the acid, so the strength of the acids (Table 11.7) increases as follows:



Oxoacids

Oxoacids (see Section 0.3) contain hydrogen, oxygen, and one other element Z, which occupies a central position. Figure 11.9 shows the Lewis structures of several common oxoacids. As you can see, these acids are characterized by the presence



Strength of hydrohalic acids increases from HF to HI.

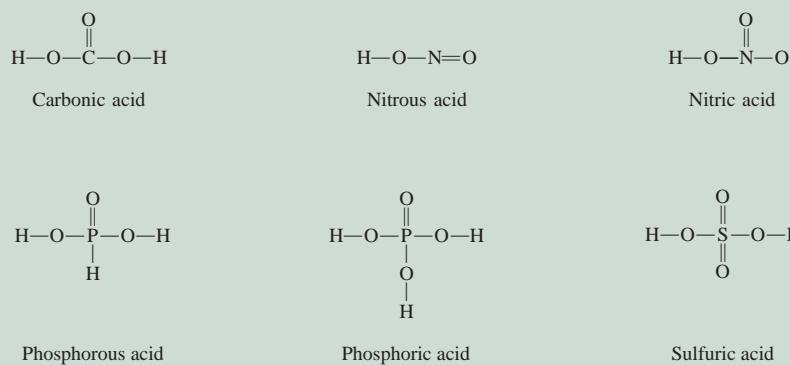
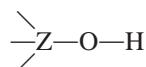


Figure 11.9 Lewis structures of some common oxoacids. For simplicity, the formal charges have been omitted.

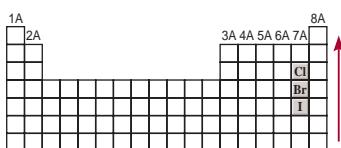
of one or more O—H bonds. The central atom Z might also have other groups attached to it:



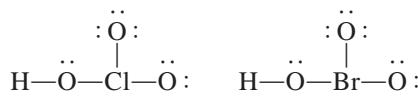
If Z is an electronegative element (such as N or S) or is bonded to several other electronegative groups, it will attract electrons, thus making the Z—O bond more covalent and the O—H bond more polar. Consequently, the tendency for the hydrogen to be donated as an H⁺ ion increases.

To compare their strengths, it helps to divide the oxoacids into two groups, those having different central atoms that are from the same group of the periodic table (and that have the same number of oxygen atoms around the central atom) and those having the same central atom but different numbers of attached groups.

1. *Oxoacids Having Different Central Atoms That Are from the Same Group of the Periodic Table and That Have the Same Number of Oxygen Atoms around the Central Atom.* The first group includes acids such as HClO₃ and HBrO₃ because both Cl and Br are from Group VIIA of the periodic table and both have the same number of oxygen atoms around the central atom:



Strength of halogen-containing oxoacids having the same number of O atoms increases from bottom to top.

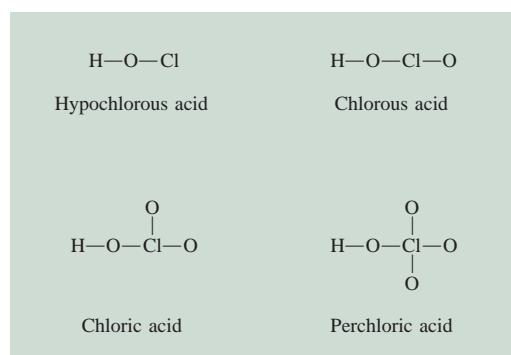


Within this group, acid strength increases with increasing electronegativity of the central atom. Cl is more electronegative than Br, so it attracts the electron pair it shares with oxygen (in the Cl—O—H group) to a greater extent than Br does. Consequently, the O—H bond is more polar in chloric acid than in bromic acid and ionizes more readily. Therefore, HClO₃ is a stronger acid than HBrO₃:

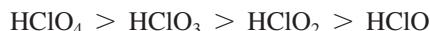


2. *Oxoacids Having the Same Central Atom but Different Numbers of Attached Groups.* The second group of acids includes the oxoacids of chlorine shown in Figure 11.10. In this series, the ability of chlorine (the central atom) to draw electrons away from the OH group (thus making the O—H bond more polar) increases with the number of electronegative O atoms attached to Cl. Thus, acid strength increases as the number of oxygen atoms around the central atom increases, making HClO₄ the strongest of these four acids (because it has the

Figure 11.10 Lewis structures of the oxoacids of chlorine.



largest number of O atoms attached to Cl) and HClO the weakest (because it has the fewest number of O atoms attached to Cl):



Example 11.16 reinforces these concepts by comparing the strengths of acids based on their molecular structures.

Example 11.16

Predict the relative strengths of the oxoacids in each of the following groups: (a) HClO, HBrO, and HIO; and (b) HNO_3 and HNO_2 .

Strategy Examine the molecular structure. In part (a) the three acids have similar structures but differ only in the central atom (the halogens Cl, Br, and I). When oxoacids have different central atoms from the same group of the periodic table and their central atoms are surrounded by the same number of oxygen atoms, the strongest acid has the most electronegative central atom. In part (b) the acids have the same central atom (N) but differ in the number of O atoms. When oxoacids have the same central atom but different numbers of attached oxygen atoms, the strongest acid has the central atom with the most oxygen atoms.

Solution (a) HClO, HBrO, and HIO all have the same structure, and the halogens (the central atoms) all have the same number of oxygen atoms around the central atom. Because the electronegativity decreases from Cl to I, the polarity of the X—O bond (where X denotes a halogen atom) increases from HClO to HIO, and the polarity of the O—H bond decreases from HClO to HIO. Thus, the acid strength decreases as follows:

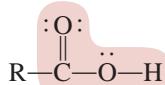


(b) The structures of HNO_3 (nitric acid) and HNO_2 (nitrous acid) are shown in Figure 11.9. Because HNO_3 has more oxygen atoms around the nitrogen atom than HNO_2 , HNO_3 is a stronger acid than HNO_2 .

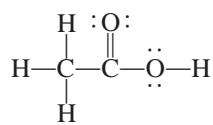
Practice Exercise Which of the following acids is weaker: H_3PO_3 or H_3PO_4 ?

Carboxylic Acids

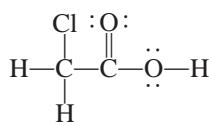
The discussion so far has focused on inorganic acids. A group of organic acids that also deserves attention is the carboxylic acids, whose Lewis structures can be generalized as follows:



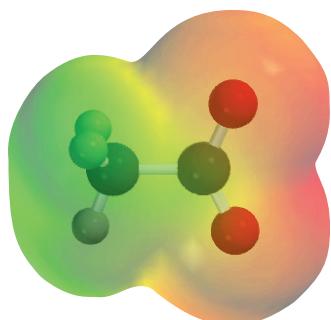
where R is part of the acid molecule and the shaded portion represents the *carboxyl* group ($-\text{COOH}$). The strengths of carboxylic acids depend on the nature of the R group. Consider, for example, acetic acid and chloroacetic acid:



acetic acid ($K_a = 1.8 \times 10^{-5}$)



chloroacetic acid ($K_a = 1.4 \times 10^{-3}$)

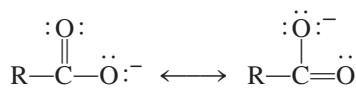


Electrostatic potential map of the acetate ion. The electron density is evenly distributed between the two O atoms.

The presence of the Cl atom in chloroacetic acid shifts electron density toward the R group because Cl is more electronegative than H, thereby making the O—H bond more polar. Consequently, there is a greater tendency for the acid to ionize:



The conjugate base of the carboxylic acid, called the carboxylate anion (RCOO^-), can exhibit resonance:



In the language of molecular orbital theory, we attribute the stability of the anion to its ability to spread or delocalize the electron density over several atoms. The greater the extent of electron delocalization, the more stable the anion and the greater the tendency for the acid to ionize. Thus, benzoic acid (C_6H_5COOH , $K_a = 6.5 \times 10^{-5}$) is a stronger acid than acetic acid because the benzene ring (see pages 260–261) facilitates electron delocalization, so that the benzoate anion ($C_6H_5COO^-$) is more stable than the acetate anion (CH_3COO^-).

11.6 | Many Salts Have Acid-Base Properties in Aqueous Solution

As defined in Section 11.1, a salt is an ionic compound formed by the reaction between an acid and a base. Salts are strong electrolytes that completely dissociate into ions in water. The term *salt hydrolysis* describes *the reaction of an anion or a cation of a salt, or both, with water*. Salt hydrolysis may produce neutral solutions, basic solutions, or acidic solutions, depending on the salt.

The word *hydrolysis* is derived from the Greek words *hydro*, meaning “water,” and *lysis*, meaning “to split apart.”

In reality, all positive ions give acidic solutions in water

Salts That Produce Neutral Solutions

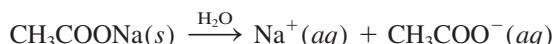
It is generally true that salts containing an alkali metal ion or alkaline earth metal ion (except Be^{2+}) and the conjugate base of a strong acid (for example, Cl^- , Br^- , and NO_3^-) do not undergo hydrolysis to an appreciable extent, and their solutions are assumed to be neutral. For instance, when NaNO_3 , a salt formed by the reaction of NaOH with HNO_3 , dissolves in water, it dissociates completely as follows:



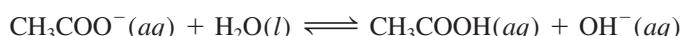
The hydrated Na^+ ion neither donates nor accepts H^+ ions. The NO_3^- ion is the conjugate base of the strong acid HNO_3 , and it has no affinity for H^+ ions. Consequently, a solution containing Na^+ and NO_3^- ions is neutral, with a pH of about 7.

Salts That Produce Basic Solutions

The solution of a salt derived from a strong base and a weak acid is basic. For example, the dissociation of sodium acetate (CH_3COONa) in water is given by



The hydrated Na^+ ion has no acidic or basic properties. The acetate ion (CH_3COO^-), however, is the conjugate base of the weak acid CH_3COOH and therefore has an affinity for H^+ ions. The hydrolysis reaction is given by



Because this reaction produces OH^- ions, the sodium acetate solution will be basic.

The equilibrium constant for this hydrolysis reaction is the base ionization constant expression for CH_3COO^- , so we use Equation 11.13 to write

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

Because each CH_3COO^- ion that hydrolyzes produces one OH^- ion, the concentration of OH^- at equilibrium is the same as the concentration of CH_3COO^- that hydrolyzed. We can define the *percent hydrolysis* as

$$\begin{aligned}\% \text{ hydrolysis} &= \frac{[\text{CH}_3\text{COO}^-]_{\text{hydrolyzed}}}{[\text{CH}_3\text{COO}^-]_{\text{initial}}} \times 100\% \\ &= \frac{[\text{OH}^-]_{\text{equilibrium}}}{[\text{CH}_3\text{COO}^-]_{\text{initial}}} \times 100\%\end{aligned}$$

A calculation based on the hydrolysis of CH_3COONa is illustrated in Example 11.17. In solving salt hydrolysis problems, we follow the same procedure we used for weak acids and weak bases.

Example 11.17

Calculate the pH of a 0.15 M solution of sodium acetate (CH_3COONa). What is the percent hydrolysis?

Strategy In solution, the salt CH_3COONa dissociates completely into Na^+ and CH_3COO^- ions. The Na^+ ion, as we saw earlier, does not react with water and has no effect on the pH of the solution. The CH_3COO^- ion is the conjugate base of the weak acid CH_3COOH . Therefore, we expect that it will react to a certain extent with water to produce CH_3COOH and OH^- , and the solution will be basic.

Solution

Step 1: Determine initial ion concentrations: Because we started with a 0.15 M sodium acetate solution, the concentrations of the ions (Na^+ and CH_3COO^-) are also equal to 0.15 M after dissociation. Of these ions, only the acetate ion will react with water:



At equilibrium, the major species in solution are CH_3COOH , CH_3COO^- , and OH^- . The concentration of the H^+ ion is very small (as we would expect for a basic solution), so it is treated as a minor species. We ignore the ionization of water.

Step 2: Determine equilibrium concentrations: Because CH_3COO^- is a weak base ($K_b = 5.6 \times 10^{-10}$), we can find the concentrations of CH_3COOH , CH_3COO^- , and OH^- using the methods in Section 11.4. From Equation 11.13 we have

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{x^2}{0.15 - x} = 5.6 \times 10^{-10}$$

—Continued

Continued—

where x represents the equilibrium concentrations of CH_3COOH and OH^- . Because K_b is very small and the initial concentration of the base is large, we can apply the approximation $0.15 - x \approx 0.15$:

$$5.6 \times 10^{-10} = \frac{x^2}{0.15 - x} \approx \frac{x^2}{0.15}$$

$$x = 9.2 \times 10^{-6} M$$

The value of x is much less than 5 percent of the initial concentration ($0.15 M$), so our approximation is justified.

Step 3: Determine the pH: At equilibrium,

$$[\text{OH}^-] = 9.2 \times 10^{-6} M$$

so

$$\begin{aligned}\text{pOH} &= -\log_{10}(9.2 \times 10^{-6}) \\ &= 5.04\end{aligned}$$

and

$$\begin{aligned}\text{pH} &= 14.00 - 5.04 \\ &= 8.96\end{aligned}$$

Thus, the solution is basic, as we would expect. The percent hydrolysis is given by

$$\begin{aligned}\% \text{ hydrolysis} &= \frac{9.2 \times 10^{-6} M}{0.15 M} \times 100\% \\ &= 0.0061\%\end{aligned}$$

Check The result shows that only a very small amount of the anion undergoes hydrolysis, as expected for a weak base.

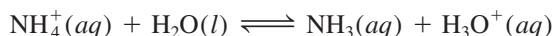
Practice Exercise Calculate the pH of a $0.24 M$ solution of sodium formate (HCOONa).

Salts That Produce Acidic Solutions

When a salt derived from a strong acid such as HCl and a weak base such as NH_3 dissolves in water, the solution becomes acidic. For example, consider the process



The Cl^- ion, being the conjugate base of a strong acid, has no affinity for H^+ and no tendency to hydrolyze. The ammonium ion (NH_4^+) is the conjugate acid of the weak base NH_3 and ionizes as follows:



Because hydronium ions are produced, the pH of the solution decreases. The equilibrium constant (or ionization constant) for this process is given by

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

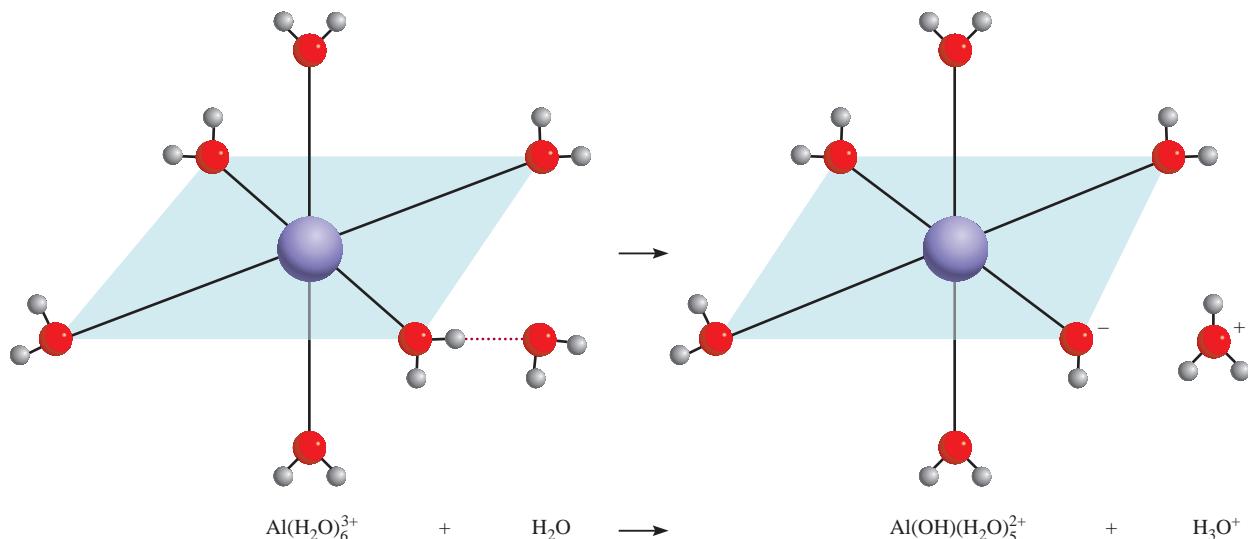


Figure 11.11 The six H_2O molecules surround the Al^{3+} ion octahedrally. The attraction of the small Al^{3+} ion for the lone pairs on the oxygen atoms is so great that the O—H bonds in an H_2O molecule attached to the metal cation are weakened, facilitating the loss of a proton (H^+) to an incoming H_2O molecule. This hydrolysis of the metal cation makes the solution acidic.

and we can calculate the pH of an ammonium chloride solution following the same procedure used in Example 11.17.

In principle, *all* metal ions react with water to produce an acidic solution. However, because the extent of hydrolysis is most pronounced for the small and highly charged metal cations such as Al^{3+} , Cr^{3+} , Fe^{3+} , Bi^{3+} , and Be^{3+} , we generally neglect the relatively small interaction of alkali metal ions and most alkaline earth metal ions with water. When aluminum chloride (AlCl_3) dissolves in water, the Al^{3+} ions act as Lewis acids to accept lone electron pairs from the water oxygen to generate the hydrated form, $\text{Al}(\text{H}_2\text{O})_6^{3+}$, shown in Figure 11.11.

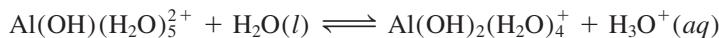
Consider one bond between the metal ion and an oxygen atom from one of the six water molecules in $\text{Al}(\text{H}_2\text{O})_6^{3+}$. The positively charged Al^{3+} ion draws electron density toward itself, increasing the polarity of the O—H bonds. Consequently, the H atoms have a greater tendency to ionize than those in water molecules not involved in hydration. The resulting ionization process can be written as



The equilibrium constant for the metal cation hydrolysis is given by

$$K_a = \frac{[\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}][\text{H}_3\text{O}^+]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]} = 1.3 \times 10^{-5}$$

$\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}$ can undergo further ionization,



until all six water molecules are ionized. However, it is generally sufficient to take into account only the first stage of hydrolysis.

The extent of hydrolysis is greatest for the smallest and most highly charged ions because a “compact” highly charged ion more effectively polarizes the O—H bond,

thus facilitating ionization. This is why relatively large ions of low charge such as Na^+ and K^+ do not undergo appreciable hydrolysis.

Salts in Which Both the Cation and the Anion Hydrolyze

So far, we have considered salts in which only one ion undergoes hydrolysis. For salts derived from a weak acid and a weak base, both the cation and the anion hydrolyze. However, whether a solution containing such a salt is acidic, basic, or neutral depends on the relative strengths of the weak acid and the weak base. Because the mathematics associated with this type of system are rather involved, we will focus on making qualitative predictions about these solutions based on the following guidelines:

- ▶ $K_b > K_a$. If K_b for the anion is greater than K_a for the cation, then the solution must be basic because the anion will hydrolyze to a greater extent than the cation. At equilibrium, there will be more OH^- ions than H^+ ions.
- ▶ $K_b < K_a$. Conversely, if K_b for the anion is smaller than K_a for the cation, the solution will be acidic because cation hydrolysis will be more extensive than anion hydrolysis.
- ▶ $K_b \approx K_a$. If K_a is approximately equal to K_b , the solution will be nearly neutral.

The calculation of the pH of a salt in which both the anion and cation hydrolyze is complicated. There are six ion concentrations that must be determined—that of the anion and its conjugate acid, the cation and its conjugate base, $[\text{H}_3\text{O}^+]$, and $[\text{OH}^-]$. The procedure for this is similar to the calculation of the pH for dilute weak acids (Section 11.4). To solve for these six concentrations, six equations are necessary: Three of these equations come from the equilibrium expressions for K_a of the cation, K_b for the anion, and K_w for water. The other three equations come from ensuring charge neutrality and material balance for both the cation- and anion-derived species. Table 11.8 summarizes the behavior in aqueous solution of the salts discussed in this section.

Example 11.18 shows how to predict the acid-base properties of salt solutions.

Example 11.18

Predict whether the following solutions will be acidic, basic, or nearly neutral: (a) NH_4I , (b) NaNO_2 , (c) FeCl_3 , and (d) NH_4F .

Strategy In deciding whether a salt will undergo hydrolysis, ask yourself the following questions: Is the cation a highly charged metal ion or the conjugate acid of a weak base

—Continued

Table 11.8 Acid-Base Properties of Salts

| Type of Salt | Examples | Ions That Undergo Hydrolysis | pH of Solution |
|--|---|------------------------------|--|
| Cation from strong base; anion from strong acid | NaCl , KI , KNO_3 , RbBr , BaCl_2 | None | ≈ 7 |
| Cation from strong base; anion from weak acid | CH_3COONa , KNO_2 | Anion | >7 |
| Cation from weak base, anion from strong acid | NH_4Cl , NH_4NO_3 | Cation | <7 |
| Cation from weak base; anion from weak acid | NH_4NO_2 , $\text{CH}_3\text{COONH}_4$, NH_4CN | Anion and cation | <7 if $K_b < K_a$ ≈ 7 if $K_b \approx K_a$ >7 if $K_b > K_a$ |
| Small, highly charged cation; anion from strong acid | AlCl_3 , $\text{Fe}(\text{NO}_3)_3$ | Hydrated cation | <7 |

Continued—

(such as the ammonium ion)? Is the anion the conjugate base of a weak acid? If the answer is yes to either question, then hydrolysis will occur. In cases where both the cation and the anion react with water, the pH of the solution will depend on the relative magnitudes of K_a for the cation and K_b for the anion (see Tables 11.3 through 11.5).

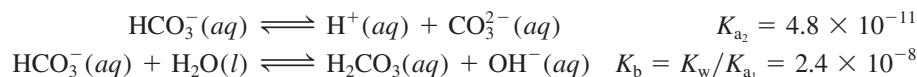
Solution We first break up the salt into its cation and anion components and then examine the possible reaction of each ion with water.

- The cation is NH_4^+ , which will hydrolyze to produce NH_3 and H_3O^+ . The I^- anion is the conjugate base of the strong acid HI . Therefore, I^- will not hydrolyze and the solution is acidic.
- The Na^+ cation does not hydrolyze to any appreciable extent. The NO_2^- anion is the conjugate base of the weak acid HNO_2 and will hydrolyze to give HNO_2 and OH^- . The solution will be basic.
- Fe^+ is a small metal ion with a high charge and hydrolyzes to produce H_3O^+ ions. The Cl^- ion does not hydrolyze because it is the conjugate base of a strong acid (HCl). The solution, therefore, will be acidic.
- Both the NH_4^+ and F^- ions will hydrolyze. According to Table 11.5, the K_a of NH_4^+ (5.6×10^{-10}) is greater than the K_b for F^- (1.4×10^{-11}). Therefore, the solution will be acidic.

Practice Exercise Predict whether the following solutions will be acidic, basic, or nearly neutral: (a) LiClO_4 , (b) Na_3PO_4 , (c) $\text{Bi}(\text{NO}_3)_2$, and (d) NH_4CN .

Salts of Amphoteric Ions

Some anions are amphoteric, that is, they can act as either an acid or a base. For example, the bicarbonate ion (HCO_3^-) can ionize or undergo hydrolysis as follows (see Table 11.6):



where K_{a_1} and K_{a_2} are the first and second ionization constants, respectively, for the diprotic acid H_2CO_3 . Because $K_b > K_a$, the hydrolysis reaction will outweigh the ionization process. Thus, a solution of sodium bicarbonate (NaHCO_3) will be basic.

A full calculation of the pH of amphoteric ion salts is complicated. To determine the H^+ concentration, we must take into account the acid and base equilibria, the autoionization of water, and the charge and material balance—five equations in all for the five unknown concentrations ($[\text{H}^+]$, $[\text{OH}^-]$, $[\text{CO}_3^{2-}]$, $[\text{HCO}_3^-]$, and $[\text{H}_2\text{CO}_3]$). With a few approximations, however, it can be shown that the pH of an amphoteric salt can be approximated by

$$\text{pH} \approx \frac{\text{p}K_{a_1} + \text{p}K_{a_2}}{2} \quad (11.27)$$

For the bicarbonate solution mentioned previously, the $\text{p}K_a$ values calculated from the K_a values in Table 11.6 are $\text{p}K_{a_1} = 6.38$ and $\text{p}K_{a_2} = 10.32$, so Equation 11.27 gives

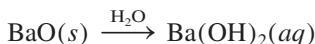
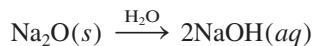
$$\text{pH} = \frac{6.38 + 10.32}{2} \approx 8.35$$

The solution is basic, consistent with the conclusion drawn previously from the relative sizes of K_{a_2} and $K_b = K_w/K_{a_1}$.

11.7 Oxide and Hydroxide Compounds Can Be Acidic or Basic in Aqueous Solution Depending on Their Composition

Oxides can be generally classified as acidic, basic, or amphoteric. Our discussion of acid-base reactions would be incomplete if we did not examine the properties of these compounds. Figure 11.12 shows the formulas of a number of oxides of the representative elements. All alkali metal oxides and all alkaline earth metal oxides except BeO are basic. Beryllium oxide and several metallic oxides in Groups 3A and 4A are amphoteric. Nonmetallic oxides in which the number of oxygen atoms around a central representative element is high are acidic (e.g., N_2O_5 , SO_3 , and Cl_2O_7), but those in which the number of oxygen atoms is low (e.g., CO and NO) show no measurable acidic properties. No nonmetallic oxides are known to have basic properties.

The basic metallic oxides react with water to form metal hydroxides:



The reactions between acidic oxides and water are as follows:

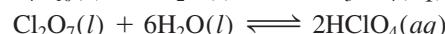
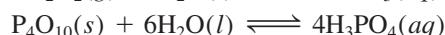
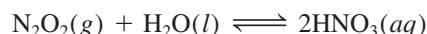
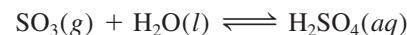
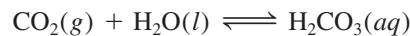


Figure 11.12 Oxides of the representative elements. For many elements, more than one oxide exists. For such elements, only the oxide with the largest number of attached oxygen atoms is shown.

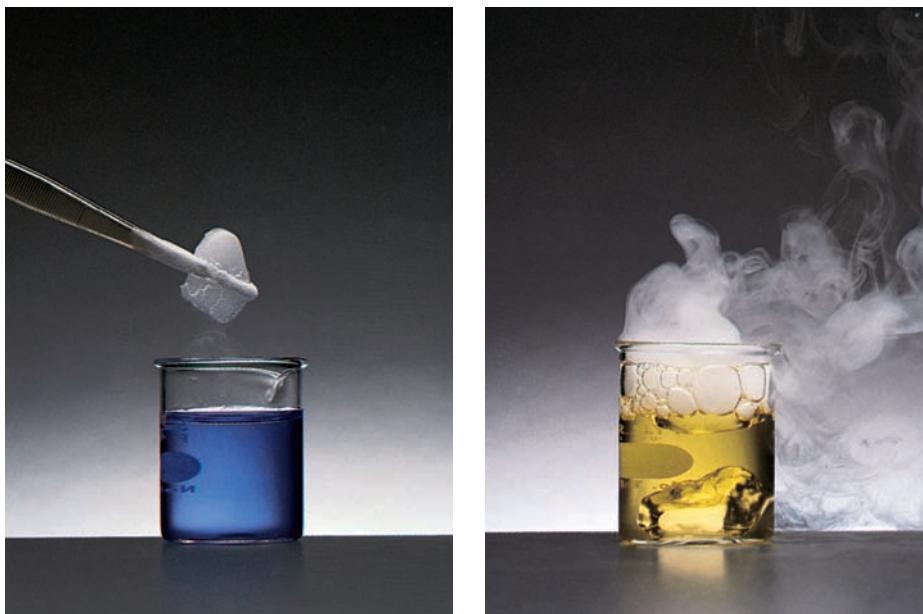
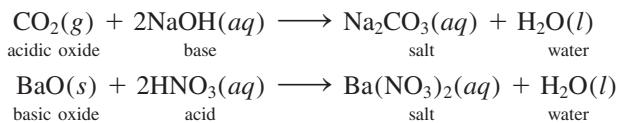


Figure 11.13 (Left) A beaker of water to which a few drops of bromothymol blue indicator have been added. (Right) As dry ice is added to the water, the CO₂ reacts to form carbonic acid, which turns the solution acidic and changes the color from blue to yellow.

The reaction between CO₂ and H₂O explains why when pure water is exposed to air (which contains CO₂), it gradually reaches a pH of about 5.5 (Figure 11.13). The reaction between SO₃ and H₂O is largely responsible for acid rain (Figure 11.14).

Reactions between acidic oxides and bases and those between basic oxides and acids resemble normal acid-base reactions in that the products are a salt and water:



Aluminum oxide (Al₂O₃) is amphoteric (see Figure 11.12). Depending on the reaction conditions, it can behave as either an acidic oxide or a basic oxide. For example, Al₂O₃ acts as a base with hydrochloric acid to produce a salt (AlCl₃) and water:



and acts as an acid with sodium hydroxide:



Only a salt, NaAl(OH)₄ [containing the Na⁺ and Al(OH)₄⁻ ions], is formed in the latter reaction; no water is produced. Nevertheless, this can still be classified as an acid-base reaction because Al₂O₃ neutralizes NaOH.

Some transition metal oxides in which the oxygen to metal atom ratio is large are acidic. Two examples are manganese(VII) oxide (Mn₂O₇) and chromium(VI) oxide (CrO₃), both of which react with water to produce acids:

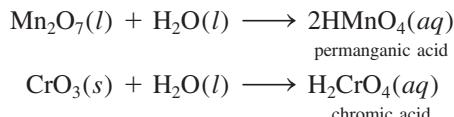
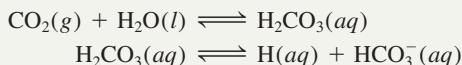


Figure 11.14 A forest damaged by acid rain.

Antacids and the pH Balance in Your Stomach

An average adult produces between 2 and 3 L of gastric juice daily. Gastric juice is a thin, acidic digestive fluid secreted by glands in the mucous membrane that lines the stomach. It contains hydrochloric acid, among other substances. The pH of gastric juice is about 1.5, which corresponds to a hydrochloric acid concentration of 0.03 M—a concentration strong enough to dissolve zinc metal! What is the purpose of this highly acidic medium? Where do the H⁺ ions come from? What happens when there is an excess of H⁺ ions present in the stomach?

A simplified diagram of the stomach is shown on the right. The inside lining is made up of parietal cells, which are fused together to form tight junctions. The interiors of the cells are protected from the surroundings by cell membranes. These membranes allow water and neutral molecules to pass in and out of the stomach, but they usually block the movement of ions such as H⁺, Na⁺, K⁺, and Cl⁻. The H⁺ ions come from carbonic acid (H₂CO₃) formed as a result of the hydration of CO₂, an end product of metabolism:

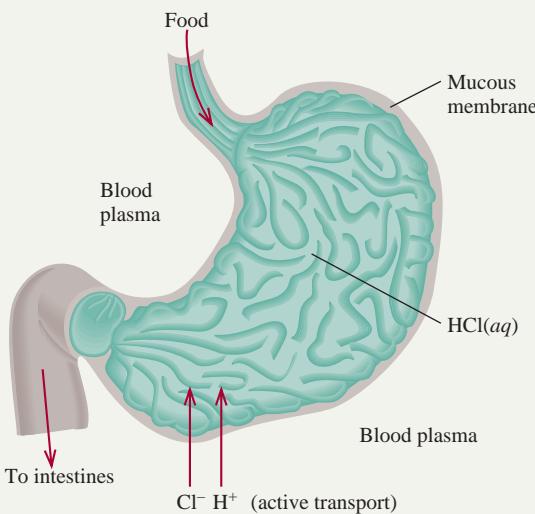


These reactions take place in the blood plasma bathing the cells in the mucosa. By a process known as *active transport*, H⁺ ions move across the membrane into the stomach interior. (Active transport processes are aided by enzymes.) To maintain electrical balance, an equal number of Cl⁻ ions also move from the blood plasma into the stomach. Once in the stomach, most of these ions are prevented from diffusing back into the blood plasma by cell membranes.

The purpose of the highly acidic medium within the stomach is to digest food and to activate certain digestive enzymes. Eating stimulates H⁺ ion secretion. A small fraction

of these ions normally are reabsorbed by the mucosa, causing many tiny hemorrhages. About half a million cells are shed by the lining every minute, and a healthy stomach is completely relined every three days or so. If the acid content is excessively high, however, the constant influx of H⁺ ions through the membrane back to the blood plasma can cause muscle contraction, pain, swelling, inflammation, and bleeding.

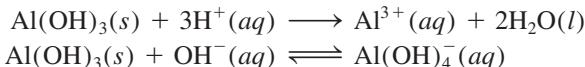
One way to temporarily reduce the H⁺ ion concentration in the stomach is to take an antacid. The major function of antacids is to neutralize excess HCl in gastric juice. The table on page 603 lists the active ingredients of some popular antacids.



A simplified diagram of the human stomach.

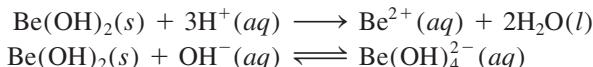
Basic and Amphoteric Hydroxides

The alkali and alkaline earth metal hydroxides [except for Be(OH)₂] have basic properties. The following hydroxides are amphoteric: Be(OH)₂, Al(OH)₃, Sn(OH)₂, Pb(OH)₂, Cr(OH)₃, Cu(OH)₂, Zn(OH)₂, and Cd(OH)₂. For example, aluminum hydroxide reacts with both acids and bases:



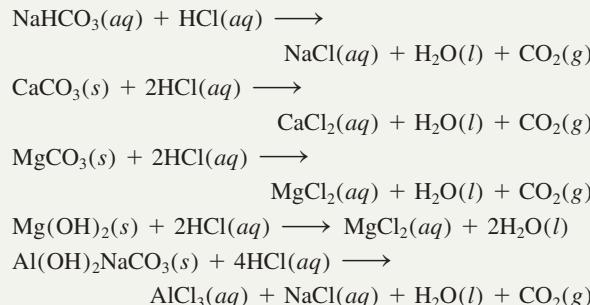
All amphoteric hydroxides are insoluble in water.

Beryllium hydroxide, like aluminum hydroxide, exhibits amphotерism:



This is another example of the diagonal relationship between beryllium and aluminum (see Section 2.5).

The reactions by which these antacids neutralize stomach acid are as follows:

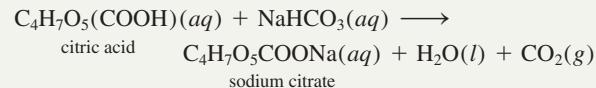


Some Common Commercial Antacid Preparations

| Commercial Name | Active Ingredients |
|------------------|--|
| Alka-2 | Calcium carbonate |
| Alka-Seltzer | Aspirin, sodium bicarbonate, citric acid |
| Bufferin | Aspirin, magnesium carbonate, aluminum glycinate |
| Buffered aspirin | Aspirin, magnesium carbonate, aluminum hydroxide-glycine |
| Milk of magnesia | Magnesium hydroxide |
| Rolaids | Dihydroxy aluminum sodium carbonate |
| Tums | Calcium carbonate |

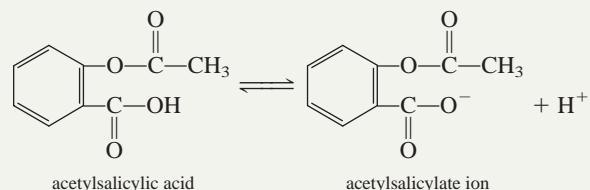
The CO_2 released by most of these reactions increases gas pressure in the stomach, causing the person to belch. The fizzing that takes place when an Alka-Seltzer tablet dissolves

in water is caused by carbon dioxide, which is released by the reaction between citric acid and sodium bicarbonate:



This action helps to disperse the ingredients and even enhances the taste of the solution.

The mucosa of the stomach can be damaged by the action of aspirin, the chemical name of which is acetylsalicylic acid. Aspirin is itself a moderately weak acid:



In the presence of the high concentration of H^+ ions in the stomach, this acid remains largely nonionized. A relatively nonpolar molecule, acetylsalicylic acid has the ability to penetrate membrane barriers that are also made up of nonpolar molecules. However, inside the membrane are many small water pockets, and when an acetylsalicylic acid molecule enters such a pocket, it ionizes into H^+ and acetylsalicylate ions. These ionic species become trapped in the interior regions of the membrane. The continued buildup of ions in this fashion weakens the structure of the membrane and eventually causes bleeding. Approximately 2 mL of blood are usually lost for every aspirin tablet taken, an amount not generally considered harmful. However, the action of aspirin can result in severe bleeding in some individuals. The presence of alcohol makes acetylsalicylic acid even more soluble in the membrane, and so further promotes the bleeding.

Summary of Facts and Concepts

Section 11.1

- ▶ Arrhenius acids ionize in water to give H^+ ions, and Arrhenius bases ionize in water to give OH^- ions.
- ▶ Brønsted acids donate protons, and Brønsted bases accept protons. These are the definitions that normally underlie the use of the terms *acid* and *base*.
- ▶ The reaction of an acid and a base is called neutralization.

- ▶ Lewis acids accept pairs of electrons and Lewis bases donate pairs of electrons. The term *Lewis acid* is generally reserved for substances that can accept electron pairs but do not contain ionizable hydrogen atoms.

Section 11.2

- ▶ The equilibrium constant for the autoionization of water is 1.0×10^{-14} at 25°C .

- The acidity of an aqueous solution is expressed as its pH, which is defined as the negative logarithm of the hydrogen ion activity. In a dilute solution the hydrogen ion activity can be well approximated by the numerical value of the hydrogen ion concentration in mol L⁻¹.
- At 25°C, an acidic solution has pH < 7, a basic solution has pH > 7, and a neutral solution has pH = 7.

Section 11.3

- In aqueous solution, the following are classified as strong acids: HClO₄, HI, HBr, HCl, H₂SO₄ (first stage of ionization), and HNO₃. Strong bases in aqueous solution include hydroxides of alkali metals and of alkaline earth metals (except beryllium).
- The acid ionization constant K_a increases with acid strength. K_b similarly expresses the strengths of bases.

Section 11.4

- Percent ionization is another measure of the strength of acids. The more dilute a solution of a weak acid, the greater the percent ionization of the acid.

Key Words

| | |
|-----------------------------------|----------------------------------|
| acid, p. 557 | Brønsted base, p. 558 |
| acid ionization constant, p. 571 | conjugate acid-base pair, p. 561 |
| amphoteric, p. 560 | diprotic acid, p. 559 |
| autoionization of water, p. 564 | hydronium ion, p. 558 |
| base, p. 557 | ion-product constant, p. 565 |
| base ionization constants, p. 573 | Lewis acid, p. 562 |
| Brønsted acid, p. 558 | Lewis base, p. 562 |

- The product of the ionization constant of an acid and the ionization constant of its conjugate base is equal to the ion-product constant of water.

Section 11.5

- The relative strengths of acids can be explained qualitatively in terms of their molecular structures.

Section 11.6

- Most salts are strong electrolytes that dissociate completely into ions in solution. The reaction of these ions with water, called salt hydrolysis, can produce acidic or basic solutions. In salt hydrolysis, the conjugate bases of weak acids yield basic solutions, and the conjugate acids of weak bases yield acidic solutions.
- Small, highly charged metal ions, such as Al³⁺ and Fe³⁺, hydrolyze to yield acidic solutions.

Section 11.7

- Most oxides can be classified as acidic, basic, or amphoteric. Metal hydroxides are either basic or amphoteric.

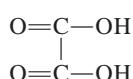
Problems

Many Processes in Chemistry Are Acid-Base Reactions

- 11.1 Classify each of the following species as a Brønsted acid, a Brønsted base, or both: (a) H₂O, (b) OH⁻, (c) H₃O, (d) NH₃, (e) NH₄⁺, (f) NH₂⁻, (g) NO₃⁻, (h) CO₂ (i) HBr, and (j) HCN.
- 11.2 Write the formulas of the conjugate bases of the following acids: (a) HNO₂, (b) H₂SO₄, (c) H₂S, (d) HCN, and (e) HCOOH (formic acid).
- 11.3 Identify the acid-base conjugate pairs in each of the following reactions:
- CH₃COO⁻ + HCN \rightleftharpoons CH₃COOH + CN⁻
 - HCO₃⁻ + HCO₃⁻ \rightleftharpoons H₂CO₃ + CO₃²⁻
 - H₂PO₄⁻ + NH₃ \rightleftharpoons HPO₄²⁻ + NH₄⁺
 - HClO + CH₃NH₂ \rightleftharpoons CH₃NH₃⁺ + ClO⁻
 - CO₃²⁻ + H₂O \rightleftharpoons HCO₃⁻ + OH⁻

11.4 Write the formula for the conjugate acid of each of the following bases: (a) HS⁻, (b) HCO₃⁻, (c) CO₃²⁻, (d) H₂PO₄⁻, (e) HPO₄²⁻, (f) PO₄³⁻, (g) HSO₄⁻, (h) SO₄²⁻, and (i) SO₃²⁻.

11.5 Oxalic acid (C₂H₂O₄) has the following structure:



An oxalic acid solution contains the following species in varying concentrations: C₂H₂O₄, C₂HO₄⁻, C₂O₄²⁻, and H⁺. (a) Draw Lewis structures of C₂HO₄⁻ and C₂O₄²⁻. (b) Which of the four species in an oxalic acid solution can act only as acids, which can act only as bases, and which can act as both acids and bases?

- 11.6 Write the formula for the conjugate base of each of the following acids: (a) CH_2ClCOOH , (b) HIO_4 , (c) H_3PO_4 , (d) H_2PO_4^- (e) HPO_4^{2-} (f) H_2SO_4 , (g) HSO_4^- , (h) HIO_3 , (i) HSO_3^- (j) NH_4^+ , (k) H_2S , (l) HS^- , and (m) HClO_3 .

- 11.7 Classify each of the following species as a Lewis acid or a Lewis base: (a) CO_2 , (b) H_2O , (c) I^- , (d) SO_2 , (e) NH_3 , (f) OH^- , (g) H^+ , and (h) BCl_3 .

- 11.8 Describe the following reaction in terms of the Lewis theory of acids and bases:



- 11.9 Which would be considered a stronger Lewis acid: (a) BF_3 or BCl_3 , and (b) Fe^{2+} or Fe^{3+} ? Explain.
- 11.10 All Brønsted acids are Lewis acids, but not all Lewis acids are Brønsted acids. Give two examples of Lewis acids that are not Brønsted acids.

The Acid-Base Properties of Aqueous Solutions Are Governed by the Autoionization Equilibrium of Water

- 11.11 The pH of a solution is 6.7. From this statement alone, can you conclude that the solution is acidic? If not, what additional information would you need?
- 11.12 Can the pH of a solution be zero or negative? If so, give examples to illustrate these values.
- 11.13 Calculate the concentration of OH^- ions in a $1.4 \times 10^{-3} M$ HCl solution at 25°C .
- 11.14 Calculate the concentration of H^+ ions in a $0.62 M$ NaOH solution at 25°C .
- 11.15 Calculate the pH of each of the following solutions at 25°C : (a) $0.0010 M$ HCl, and (b) $0.76 M$ KOH.
- 11.16 Calculate the pH of each of the following solutions at 25°C : (a) $2.8 \times 10^{-4} M$ $\text{Ba}(\text{OH})_2$, and (b) $5.2 \times 10^{-4} M$ HNO_3 .
- 11.17 Calculate the hydrogen ion concentration in mol L^{-1} for solutions with the following pH values at 25°C : (a) 2.42, (b) 11.21, (c) 6.96, and (d) 15.00.
- 11.18 Calculate the hydrogen ion concentration in mol L^{-1} for each of the following solutions at 25°C : (a) a solution whose pH is 5.20, (b) a solution whose pH is 16.00, and (c) a solution whose hydroxide ion concentration is $3.7 \times 10^{-9} M$.
- 11.19 The pOH of a solution is 9.40 at 25°C . Calculate the hydrogen ion concentration of the solution.
- 11.20 Calculate the number of moles of KOH in 5.50 mL of a $0.360 M$ KOH solution at 25°C . What is the pOH of the solution?
- 11.21 How much NaOH (in grams) is needed to prepare 546 mL of solution with a pH of 10.00 at 25°C ?
- 11.22 A solution is made by dissolving 18.4 g of HCl in 662 mL of water. Calculate the pH of the solution at 25°C . (Assume that the volume remains constant.)

- 11.23 For which of the following solutions would you expect the measured value of the pH to differ most from the pH calculated from the H^+ ion concentration: (a) a $2.0 \times 10^{-5} M$ solution of HCl, (b) a $0.1 M$ solution of HNO_3 , and (c) a $0.00050 M$ solution of NaOH?

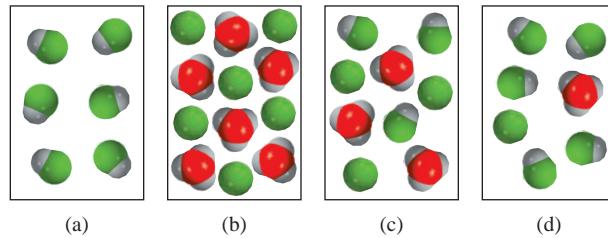
- 11.24 For which of the following solutions would you expect the measured value of the pH to differ most from the pH calculated from the H^+ ion concentration: (a) a $5.0 \times 10^{-4} M$ solution of KOH, (b) a $4.7 \times 10^{-6} M$ solution of HCl, and (c) a $0.0560 M$ solution of NaOH?

- 11.25 An aqueous solution at 60°C has an H^+ concentration of $1.5 \times 10^{-5} M$. What is the OH^- concentration of this solution?

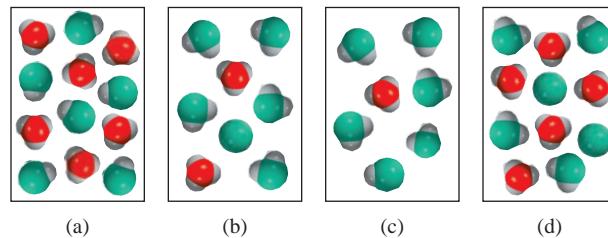
- 11.26 What is the pH of an aqueous solution at 40°C that has a pOH of 4.5?

The Strengths of Acids and Bases Are Measured by Their Ionization Constants

- 11.27 Which of the following diagrams best represents a strong acid, such as HCl, dissolved in water? Which represents a weak acid? Which represents a very weak acid? (The hydrated proton is shown as a hydronium ion. Water molecules are omitted for clarity.)



- 11.28 (1) Which of the following diagrams represents a solution of a weak diprotic acid? (2) Which diagrams represent chemically implausible situations? (The hydrated proton is shown as a hydronium ion. Water molecules are omitted for clarity.)



- 11.29 Classify each of the following species as a weak or strong acid: (a) HNO_3 , (b) HF, (c) H_2SO_4 , (d) HSO_4^- , (e) H_2CO_3 , (f) HCO_3^- , (g) HCl, (h) HCN, and (i) HNO_2 .

- 11.30 Classify each of the following species as a weak or strong base: (a) LiOH, (b) CN^- , (c) H_2O , (d) ClO_4^- , and (e) NH_2^- .

- 11.31 Which of the following statements is true for a 0.10 M solution of a weak acid HA?

- (a) The pH is 1.00.
- (b) $[\text{H}^+] \gg [\text{A}]$.
- (c) $[\text{H}] = [\text{A}]$.
- (d) The pH is less than 1.

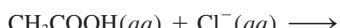
- 11.32 Which of the following statements is true regarding a 1.0 M solution of a strong acid HA?

- (a) $[\text{A}^-] > [\text{H}^+]$.
- (b) The pH is approximately zero.
- (c) $[\text{H}^+] = 1.0\text{ M}$.
- (d) $[\text{HA}] = 1.0\text{ M}$.

- 11.33 Predict the direction that predominates in the following reaction:



- 11.34 Predict whether the following reaction will proceed from left to right to any measurable extent:



- 11.35 The K_a for the weak acid HF is 7.1×10^{-4} at 25°C . Using the techniques from Chapter 10, determine the K_a for HF at 60°C . The ΔH° for the ionization of HF in aqueous solution is $-61.53\text{ kJ mol}^{-1}$.

The pH of an Acid or Base Can Be Calculated If Its Ionization Constant Is Known

- 11.36 Why do we normally not quote K_a values for strong acids such as HCl and HNO_3 ?

- 11.37 Why is it necessary to specify temperature when giving K_a values?

- 11.38 Which of the following solutions has the highest pH: (a) 0.40 M HCOOH , (b) 0.40 M HClO_4 , or (c) 0.40 M CH_3COOH ?

- 11.39 The K_a for benzoic acid is 6.5×10^{-5} . Calculate the pH of a 0.10 M benzoic acid solution.

- 11.40 A 0.0560-g quantity of acetic acid is dissolved in enough water to make 50.0 mL of solution. Calculate the concentrations of H, CH_3COO^- , and CH_3COOH at equilibrium. (K_a for acetic acid is 1.8×10^{-5} .)

- 11.41 The pH of an acid solution is 6.20. Calculate the K_a for the acid. The initial acid concentration is 0.010 M .

- 11.42 What is the original molarity of a solution of formic acid (HCOOH) whose pH is 3.26 at equilibrium?

- 11.43 Calculate the percent ionization of benzoic acid at the following concentrations: (a) 0.20 M , and (b) 0.00020 M .

- 11.44 Calculate the percent ionization of hydrofluoric acid at the following concentrations: (a) 0.60 M , (b) 0.0046 M , and (c) 0.00028 M . Comment on the trends.

- 11.45 A 0.040 M solution of a monoprotic acid is 14 percent ionized. Calculate the ionization constant of the acid.

- 11.46 (a) Calculate the percent ionization of a 0.20 M solution of the monoprotic acetylsalicylic acid (aspirin) for which $K_a = 3.0 \times 10^{-4}$. (b) The pH of gastric juice in the stomach of a certain individual is 1.00. After a few aspirin tablets have been swallowed, the concentration of acetylsalicylic acid in the person's stomach is 0.20 M . Calculate the percent ionization of the acid under these conditions. What effect does the nonionized acid have on the membranes lining the stomach? (Hint: See the essay starting on page 602)

- 11.47 Calculate the pH for each of the following solutions at 25°C : (a) 0.10 M NH_3 , and (b) 0.050 M $\text{C}_5\text{H}_5\text{N}$ (pyridine).

- 11.48 The pH of a 0.30 M solution of a weak base is 10.66. What is the K_b of the base?

- 11.49 What is the original molarity of a solution of ammonia whose pH is 11.22 at 25°C ?

- 11.50 In a 0.080 M NH_3 solution at 25°C , what percent of the NH_3 is present as NH_4^+ ?

- 11.51 Write all the species (except water) that are present in a phosphoric acid solution. Indicate which species can act as a Brønsted acid, which as a Brønsted base, and which as both a Brønsted acid and a Brønsted base.

- 11.52 (a) Compare the pH of a 0.040 M HCl solution with that of a 0.040 M H_2SO_4 solution at 25°C . (b) What are the concentrations of HSO_4^- , SO_4^{2-} , and H^+ in a 0.20 M KHSO_4 solution? (Hint: H_2SO_4 is a strong acid; K_a for HSO_4^- is 1.3×10^{-2} at 25°C .)

- 11.53 Calculate the concentrations of H^+ , HCO_3^- , and CO_3^{2-} in a 0.025 M H_2CO_3 solution at 25°C .

- 11.54 Calculate the pH of a $2.0 \times 10^{-7}\text{ M}$ solution of hydrochloric acid at 25°C .

- 11.55 Calculate the pH of a $2.0 \times 10^{-7}\text{ M}$ solution of formic acid at 25°C .

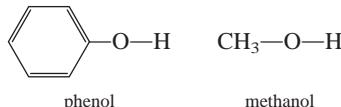
- 11.56 The first and second ionization constants of a diprotic acid H_2A are K_{a_1} and K_{a_2} at a certain temperature. Under what conditions will $[\text{A}^{2-}] = K_{a_2}$?

- 11.57 Calculate the pH of a 0.0015 M phosphoric acid solution at 25°C .

The Strength of an Acid Is Determined in Part by Molecular Structure

- 11.58 Predict the acid strengths of the following compounds: H_2O , H_2S , and H_2Se .

- 11.59 Compare the strengths of the following pairs of acids:
 (a) H_2SO_4 and H_2SeO_4 , and (b) H_3PO_4 and H_3AsO_4 .
- 11.60 Which of the following is the stronger acid: CH_2ClCOOH or CHCl_2COOH ? Explain your choice.
- 11.61 Consider phenol and methanol (both of which are alcohols):



Experimentally, phenol is found to be a stronger acid than methanol. Explain this difference in terms of the structures of the conjugate bases. (*Hint:* A more stable conjugate base favors ionization. Only one of these conjugate bases can be stabilized by resonance.)

Many Salts Have Acid-Base Properties in Aqueous Solution

- 11.62 Predict the pH (>7 , $=7$, or <7) of aqueous solutions containing the following salts: (a) KBr, (b) $\text{Al}(\text{NO}_3)_3$, (c) BaCl_2 , and (d) $\text{Bi}(\text{NO}_3)_3$.
- 11.63 Predict whether the following aqueous solutions are acidic, basic, or nearly neutral: (a) NaBr, (b) K_2SO_3 , (c) NH_4NO_2 , and (d) $\text{Cr}(\text{NO}_3)_3$.
- 11.64 A certain salt, MX (containing the M^+ and X^- ions), is dissolved in water, and the pH of the resulting solution is 7.0 at 25°C. Can you say anything about the strengths of the acid and the base from which the salt is derived?
- 11.65 In a certain experiment, a student finds that the pH values of 0.10 M solutions of three potassium salts KX, KY, and KZ are 7.0, 9.0, and 11.0, respectively. Arrange the acids HX, HY, and HZ in the order of increasing acid strength.
- 11.66 Calculate the pH of a 0.36 M CH_3COONa solution at 25°C.
- 11.67 Calculate the pH of a 0.42 M NH_4Cl solution at 25°C.
- 11.68 Predict the pH (>7 , $=7$, <7) of an NaHCO_3 solution.
- 11.69 Predict whether a solution containing the salt K_2HPO_4 will be acidic, basic, or neutral.
- 11.70 Calculate the pH of a 0.015 M oxalic acid solution at 25°C?

Oxide and Hydroxide Compounds Can Be Acidic or Basic in Aqueous Solution Depending on Their Composition

- 11.71 Arrange the oxides in each of the following groups in order of increasing basicity: (a) K_2O , Al_2O_3 , BaO , and (b) CrO_3 , CrO , Cr_2O_3 .
- 11.72 $\text{Zn}(\text{OH})_2$ is an amphoteric hydroxide. Write balanced ionic equations to show its reaction with (a) HCl, and (b) NaOH [the product is $\text{Zn}(\text{OH})_4^{2-}$].

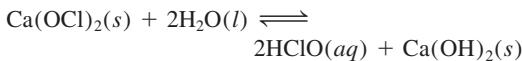
- 11.73 $\text{Al}(\text{OH})_3$ is insoluble in pure water, but it dissolves in excess NaOH in solution. Write a balanced ionic equation for this reaction. What type of reaction is this?

Additional Problems

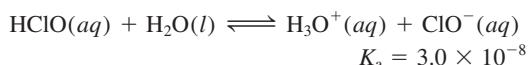
- 11.74 The K_a of formic acid is 1.7×10^{-4} at 25°C. Will the acid become stronger or weaker at 40°C? Explain.
- 11.75 A typical reaction between an antacid and the hydrochloric acid in gastric juice is
- $$\text{NaHCO}_3(s) + \text{HCl}(aq) \rightleftharpoons \text{NaCl}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g).$$
- Calculate the volume (in L) of CO_2 generated from 0.350 g of NaHCO_3 and excess gastric juice at 1.00 bar and 37.0°C.
- 11.76 To which of the following would the addition of an equal volume of 0.60 M NaOH lead to a solution having a lower pH: (a) water, (b) 0.30 M HCl, (c) 0.70 M KOH, and (d) 0.40 M NaNO_3 ?
- 11.77 The pH of a 0.0642 M solution of a monoprotic acid is 3.86 at 25°C. Is this a strong acid?
- 11.78 Like water, liquid ammonia undergoes autoionization:
- $$\text{NH}_3 + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-$$
- (a) Identify the Brønsted acids and Brønsted bases in this reaction. (b) What species correspond to H^+ and OH^- , and what is the condition for a neutral solution?
- 11.79 HA and HB are both weak acids, although HB is the stronger of the two. Will it take a larger volume of a 0.10 M NaOH solution to neutralize 50.0 mL of 0.10 M HB or 50.0 mL of 0.10 M HA?
- 11.80 A solution contains a weak monoprotic acid HA and its sodium salt NaA, both at 0.1 M concentration. Show that $[\text{OH}^-] = K_w/K_a$.
- 11.81 The three common chromium oxides are CrO , Cr_2O_3 , and CrO_3 . If Cr_2O_3 is amphoteric, what can you say about the acid-base properties of CrO and CrO₃?
- 11.82 Use the data in Appendix 2 to determine ΔH° , ΔS° , and ΔG° for the autoionization of water at 25°C. Using the techniques discussed in Chapter 10, determine the value of K_w at 25°C and at 60°C. What assumptions must you make to do these calculations? Compare your results with the data in Table 11.2.
- 11.83 Use the data in Table 11.3 to calculate the equilibrium constant for the following reaction at 25°C:
- $$\text{HCOOH}(aq) + \text{OH}^-(aq) \rightleftharpoons \text{HCOO}^-(aq) + \text{H}_2\text{O}(l)$$
- 11.84 Use the data in Table 11.3 to calculate the equilibrium constant for the following reaction at 25°C:
- $$\text{CH}_3\text{COOH}(aq) + \text{NO}_2(aq) \rightleftharpoons \text{CH}_3\text{COO}^-(aq) + \text{HNO}_2(aq)$$

- 11.85 Most of the hydrides of Group 1A and Group 2A metals are ionic (the exceptions are BeH_2 and MgH_2 , which are covalent compounds). Describe the reaction between the hydride ion (H^-) and water in terms of a Brønsted acid-base reaction.
- 11.86 The K_b for the weak base NH_3 is 1.8×10^{-5} at 25°C . Using the techniques from Chapter 10 and the data in Appendix 2, determine the K_b for NH_3 at 50°C .
- 11.87 Calculate the pH of a 0.20 M ammonium acetate ($\text{CH}_3\text{COONH}_4$) solution at 25°C .
- 11.88 Novocaine, used as a local anesthetic by dentists, is a weak base ($K_b = 8.91 \times 10^{-6}$ at 25°C). What is the ratio of the concentration of the base to that of its acid in the blood plasma (pH = 7.40) of a patient?
- 11.89 Which of the following is the stronger base: NF_3 or NH_3 ? (Hint: F is more electronegative than H.)
- 11.90 Which of the following is a stronger base: NH_3 or PH_3 ? (Hint: The N—H bond is stronger than the P—H bond.)
- 11.91 The ion product of D_2O is 1.35×10^{-15} at 25°C .
 (a) Calculate pD of neutral D_2O , where $\text{pD} = -\log_{10}[\text{D}]$. (b) For what values of pD will a solution be acidic in D_2O ? (c) Derive a relation between pD and pOD.
- 11.92 Give a physical explanation as to why D_2O should have a smaller ion product constant than H_2O at 25°C (1.35×10^{-15} for D_2O versus 1.01×10^{-14} for H_2O).
- 11.93 Give an example of (a) a weak acid that contains oxygen atoms, (b) a weak acid that does not contain oxygen atoms, (c) a neutral molecule that acts as a Lewis acid, (d) a neutral molecule that acts as a Lewis base, (e) a weak acid that contains two ionizable H atoms, and (f) a conjugate acid-base pair, both of which react with HCl to give carbon dioxide gas.
- 11.94 What is the pH of 250.0 mL of an aqueous solution containing 0.616 g of the strong acid trifluoromethane sulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$)?
- 11.95 (a) Use VSEPR to predict the geometry of the hydronium ion (H_3O^+). (b) The O atom in H_2O has two lone pairs and in principle can accept two H^+ ions. Explain why the species H_4O^{2+} does not exist. What would be its geometry if it did exist?
- 11.96 HF is a weak acid, but its strength increases with concentration. Explain. (Hint: F^- reacts with HF to form HF_2^- . The equilibrium constant for this reaction is 5.2 at 25°C .)
- 11.97 When chlorine reacts with water, the resulting solution is weakly acidic and reacts with AgNO_3 to give a white precipitate. Write balanced equations to represent these reactions. Explain why manufacturers of household bleaches add bases such as NaOH to their products to increase their effectiveness.
- 11.98 Hemoglobin (Hb) is a blood protein that is responsible for transporting oxygen. It can exist in the protonated form as HbH . The binding of oxygen can be represented by the simplified equation
- $$\text{HbH}^+ + \text{O}_2 \rightleftharpoons \text{HbO}_2 + \text{H}^+$$
- (a) What form of hemoglobin is favored in the lungs, where the oxygen concentration is highest? (b) In body tissues, where the cells release carbon dioxide produced by metabolism, the blood is more acidic due to the formation of carbonic acid. What form of hemoglobin is favored under this condition? (c) When a person hyperventilates, the concentration of CO_2 in his or her blood decreases. How does this action affect the given equilibrium? Frequently a person who is hyperventilating is advised to breathe into a paper bag. Why does this action help the individual?
- 11.99 Calculate the concentrations of all species in a 0.100 M H_3PO_4 solution at 25°C .
- 11.100 In the vapor phase, acetic acid molecules associate to a certain extent to form dimers:
- $$2\text{CH}_3\text{COOH}(g) \rightleftharpoons (\text{CH}_3\text{COOH})_2(g)$$
- At 51°C , the pressure of a certain acetic acid vapor system is 0.0346 bar in a 360-mL flask. The vapor is condensed and neutralized with 13.8 mL of 0.0568 M NaOH . (a) Calculate the degree of dissociation (α) of the dimer under these conditions:
- $$(\text{CH}_3\text{COOH})_2 \rightleftharpoons 2\text{CH}_3\text{COOH}$$
- (Hint: See Problem 10.66 for the general procedure.)
- (b) Calculate the equilibrium constant K_P for the reaction in part (a).
- 11.101 Calculate the concentrations of all the species in a 0.100 M Na_2CO_3 solution at 25°C .
- 11.102 Using Equations 11.3, 11.11, 11.23, and 11.24 as a starting point, derive the cubic equation for the H^+ ion concentration of a dilute weak acid given by Equation 11.25.
- 11.103 The Henry's law constant for CO_2 at 38°C is $2.30 \times 10^{-3}\text{ mol L}^{-1}\text{ bar}^{-1}$. Calculate the pH of a solution of CO_2 at 38°C in equilibrium with the gas at a partial pressure of 3.20 bar.
- 11.104 Hydrocyanic acid (HCN) is a weak acid and a deadly poisonous compound—in the gaseous form (hydrogen cyanide), it was used in gas chambers. Why is it dangerous to treat sodium cyanide with acids (such as HCl) without proper ventilation?
- 11.105 How many grams of NaCN would you need to dissolve in enough water to make exactly 250 mL of solution with a pH of 11.00?
- 11.106 A solution of formic acid (HCOOH) has a pH of 2.53 at 25°C . How many grams of formic acid are there in 100.0 mL of the solution?

- 11.107 Calculate the pH of a 1.0-L solution containing 0.150 mole of CH_3COOH and 0.100 mole of HCl at 25°C.
- 11.108 A 1.87-g sample of Mg reacts with 80.0 mL of an HCl solution whose pH is –0.544. What is the pH of the solution after all the Mg has reacted? Assume constant volume.
- 11.109 You are given two beakers, one containing an aqueous solution of strong acid (HA) and the other an aqueous solution of weak acid (HB) of the same concentration. Describe how you would compare the strengths of these two acids by (a) measuring the pH, (b) measuring electrical conductance, and (c) studying the rate of hydrogen gas evolution when these solutions are reacted with an active metal such as Mg or Zn.
- 11.110 Use Le Châtelier's principle to predict the effect of the following changes on the extent of hydrolysis of sodium nitrite (NaNO_2) solution: (a) HCl is added, (b) NaOH is added, (c) NaCl is added, and (d) the solution is diluted.
- 11.111 Describe the hydration of SO_2 as a Lewis acid-base reaction. (Hint: Refer to the discussion of the hydration of CO_2 on page 563.)
- 11.112 The disagreeable odor of fish is mainly due to organic compounds (RNH_2) containing an amino group, ($-\text{NH}_2$), where R is the rest of the molecule. These compounds are called amines, and they are bases just like ammonia. Explain why putting some lemon juice on fish can greatly reduce the odor.
- 11.113 A solution of methylamine (CH_3NH_2) has a pH of 10.64 at 25°C. How many grams of methylamine are there in 100.0 mL of the solution?
- 11.114 A 0.400 M formic acid (HCOOH) solution freezes at –0.758°C. Calculate the K_a of the acid at that temperature. (Hint: Assume that molarity is equal to molality. Carry your calculations to three significant figures and round off to two for K_a .)
- 11.115 Both the amide ion (NH_2^-) and the nitride ion (N^{3-}) are stronger bases than the hydroxide ion and hence do not exist in aqueous solutions. (a) Write equations showing the reactions of these ions with water, and identify the Brønsted acid and Brønsted base in each case. (b) Which of the two is the stronger base?
- 11.116 The atmospheric sulfur dioxide (SO_2) concentration over a certain region is 0.12 ppm by volume. Calculate the pH of the rainwater at 20°C due to this pollutant. Assume that the dissolution of SO_2 does not affect its pressure.
- 11.117 Calcium hypochlorite [$\text{Ca}(\text{OCl})_2$] is used as a disinfectant for swimming pools. When dissolved in water it produces hypochlorous acid,



which ionizes as follows:



As strong oxidizing agents, both HClO and ClO^- can kill bacteria by destroying their cellular components. However, too high an HClO concentration is irritating to the eyes of swimmers and too high a concentration of ClO^- will cause the ions to decompose in sunlight. The recommended pH for pool water is 7.8. Calculate the percent of these species present at this pH.

- 11.118 Explain the action of smelling salt, which is ammonium carbonate $[(\text{NH}_4)_2\text{CO}_3]$. (Hint: The thin film of aqueous solution that lines the nasal passage is slightly basic.)
- 11.119 About half of the hydrochloric acid produced annually in the United States (3.0 billion pounds) is used in metal pickling. This process involves the removal of metal oxide layers from metal surfaces to prepare them for coating. (a) Write the overall and net ionic equations for the reaction between iron(III) oxide, which represents the rust layer over iron, and HCl. Identify the Brønsted acid and Brønsted base. (b) Hydrochloric acid is also used to remove scale (which is mostly CaCO_3) from water pipes. Hydrochloric acid reacts with calcium carbonate in two stages: The first stage forms the bicarbonate ion, which then reacts further to form carbon dioxide. Write equations for these two stages and for the overall reaction. (c) Hydrochloric acid is used to recover oil from the ground. It dissolves rocks (often CaCO_3) so that the oil can flow more easily. In one process, a 15 percent (by mass) HCl solution is injected into an oil well to dissolve the rocks. If the density of the acid solution is 1.073 g mL^{-1} , what is the pH of the solution?
- 11.120 Which of the following does not represent a Lewis acid-base reaction?
- $\text{H}_2\text{O} + \text{H}^+ \longrightarrow \text{H}_3\text{O}^+$
 - $\text{NH}_3 + \text{BF}_3 \longrightarrow \text{H}_3\text{NBF}_3$
 - $\text{PF}_3 + \text{F}_2 \longrightarrow \text{PF}_5$
 - $\text{Al}(\text{OH})_3 + \text{OH}^- \longrightarrow \text{Al}(\text{OH})_4^-$
- 11.121 True or false? If false, explain why the statement is wrong. (a) All Lewis acids are Brønsted acids. (b) The conjugate base of an acid always carries a negative charge. (c) The percent ionization of a base increases with its concentration in solution. (d) A solution of barium fluoride is acidic.
- 11.122 How many milliliters of a strong monoprotic acid solution at pH = 4.12 must be added to 528 mL of the same acid solution at pH 5.76 to change its pH to 5.34? Assume that the volumes are additive.

- 11.123** A 1.294-g sample of a metal carbonate (MCO_3) is reacted with 500 mL of a 0.100 M HCl solution. The excess HCl acid is then neutralized by 32.80 mL of 0.588 M NaOH. Identify M .
- 11.124** Prove the statement that when the concentration of a weak acid HA decreases by a factor of 10, its percent ionization increases by a factor of $\sqrt{10}$. State any assumptions.
- 11.125** Calculate the pH of a solution that is 1.00 M HCN and 1.00 M HF at 25°C. Compare the concentration (in molarity) of the CN^- ion in this solution with that in a 1.00 M HCN solution. Comment on the difference.

- 11.126** Tooth enamel is largely hydroxyapatite [$Ca_5(PO_4)_3OH$]. When it dissolves in water (a process called *demineralization*), it dissociates as follows:



The reverse process, called *remineralization*, is the body's natural defense against tooth decay. Acids produced from food remove the OH^- ions and thereby weaken the enamel layer. Most toothpastes contain a fluoride compound such as NaF or SnF₂. What is the function of these compounds in preventing tooth decay?

Answers to Practice Exercises

- 11.1** (1) H_2O and OH^- . (2) HCN and CN^- . **11.2** (a) Lewis acid: C_O^{3+} , Lewis base: NH_3 ; (b) Lewis acid: BF_3 ; Lewis base: CO **11.3** $7.7 \times 10^{-11} M$ **11.4** 0.12 **11.5** $4.7 \times 10^{-4} M$ **11.6** 7.40 **11.7** 7.94, $1.1 \times 10^{-8} M$ **11.8** 5.6×10^{-10} , 2.30×10^{-11} **11.9** Smaller than 1 **11.10** 9.56 **11.11** (a) 3.32,

- (b) 2.82 **11.12** (a) 11.53, (b) 10.50 **11.13** 6.91 **11.14** 6.89 **11.15** $[H_2C_2O_2] = 0.0012 M$, $[HC_2O_4^-] = 0.0088 M$, $[C_2O_4^{2-}] = 1.5 \times 10^{-13} M$, $[H^+] = 0.0088 M$, $[OH^-] = 1.1 \times 10^{-12} M$ **11.16** H_3PO_3 **11.17** 8.58 **11.18** (a) $pH \approx 7$, (b) $pH > 7$, (c) $pH < 7$, (d) $pH > 7$

12

Chapter

Acid-Base Equilibria and Solubility



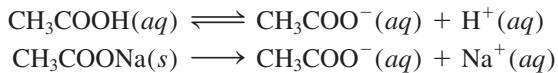
In this chapter, we will continue the study of acid-base reactions with a discussion of buffer action and titrations. We will also look at another type of aqueous equilibrium—that between slightly soluble compounds and their ions in solution.

- 12.1** The Ionization of Weak Acids and Bases Is Suppressed by the Addition of a Common Ion 612
- 12.2** The pH of a Buffer Solution Is Resistant to Large Changes in pH 615
- 12.3** The Concentration of an Unknown Acid or Base Can Be Determined by Titration 622
- 12.4** An Acid-Base Indicator Is a Substance That Changes Color at a Specific pH 631
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12.1 | The Ionization of Weak Acids and Bases Is Suppressed by the Addition of a Common Ion

Our discussion of acid-base ionization and salt hydrolysis in Chapter 11 was limited to solutions containing a single solute. In this section, we will consider the acid-base properties of a solution with two dissolved solutes that contain the same ion (cation or anion), called the *common ion*.

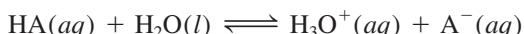
The presence of a common ion suppresses the ionization of a weak acid or a weak base. If sodium acetate and acetic acid are dissolved in the same solution, for example, they both dissociate and ionize to produce CH_3COO^- ions:



CH_3COONa is a strong electrolyte, so it dissociates completely in solution, but CH_3COOH , a weak acid, ionizes only slightly. According to Le Châtelier's principle, the addition of CH_3COO^- ions from CH_3COONa to a solution of CH_3COOH will suppress the ionization of CH_3COOH (that is, shift the equilibrium from right to left), thereby decreasing the hydrogen ion concentration. Thus, a solution containing both CH_3COOH and CH_3COONa will be *less* acidic than a solution containing only CH_3COOH at the same concentration. The shift in equilibrium of the acetic acid ionization is caused by the acetate ions from the salt. CH_3COO^- is the common ion because it is supplied by both CH_3COOH and CH_3COONa .

The **common ion effect** is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance. The common ion effect plays an important role in determining the pH of a solution and the solubility of a slightly soluble salt (to be discussed later in Section 12.7). Here we will study the common ion effect as it relates to the pH of a solution. Keep in mind that despite its distinctive name, the common ion effect is simply a special case of Le Châtelier's principle.

Let us consider the pH of a solution containing a weak acid, HA, and a soluble salt of the weak acid, such as NaA. We start by writing



or simply



The ionization constant K_a was defined in Equation 11.10:

$$K_a = \frac{a_{\text{H}_3\text{O}^+(aq)} a_{\text{A}^-(aq)}}{a_{\text{HA}(aq)} a_{\text{H}_2\text{O}(l)}}$$

If the concentrations are sufficiently low, then the activities of solutes in Equation 11.10 can be replaced with molarities (without units) and the activity of pure water can be assumed to be unity, giving (Equation 11.11)

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

Rearranging this equation gives

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

Taking the negative logarithm (base 10) of both sides, we obtain

$$-\log_{10} [\text{H}^+] = -\log_{10} K_a - \log_{10} \frac{[\text{HA}]}{[\text{A}^-]}$$

or

$$-\log_{10} [\text{H}^+] = -\log_{10} K_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$$

Using the definitions of pH (Equation 11.5) and pK_a (Equation 11.15) gives (assuming dilute solution behavior)

$$\text{pH} = pK_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]} \quad (12.1)$$

Equation 12.1 is called the **Henderson-Hasselbalch equation**. A more general form of this expression is

$$\text{pH} = pK_a + \log_{10} \frac{\text{conjugate base}}{\text{acid}} \quad (12.2)$$

Keep in mind that pK_a is a constant, but the ratio of the two concentration terms in Equation 12.2 depends upon the particular solution.

In our example, HA is the acid and A^- is the conjugate base. Thus, if we know K_a and the concentrations of the acid and the salt of the acid, we can calculate the pH of the solution.

It is important to remember that the Henderson-Hasselbalch equation is derived from the equilibrium constant expression. It is valid regardless of the source of the conjugate base (that is, whether it comes from the acid alone or is supplied by both the acid and its salt).

In problems that involve the common ion effect, we are usually given the starting concentrations of a weak acid HA and its salt, such as NaA. If the concentrations of these species are reasonably high ($> 0.1 M$), we can neglect the ionization of the acid and the hydrolysis of the salt. This is a valid approximation because HA is a weak acid and the extent of the hydrolysis of the A^- ion is generally very small. Moreover, the presence of A^- (from NaA) further suppresses the ionization of HA and the presence of HA further suppresses the hydrolysis of A^- . Thus, in such cases, we can use the *starting* concentrations as the equilibrium concentrations in Equation 12.1.

In Example 12.1 we calculate the pH of a solution containing a common ion.

Example 12.1

- (a) Calculate the pH of a solution containing $0.20 M$ CH_3COOH and $0.30 M$ CH_3COONa .
 (b) What would the pH of a $0.20 M$ CH_3COOH solution be if no salt were present?

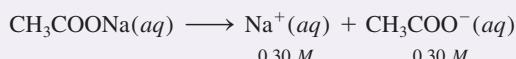
Strategy (a) CH_3COOH is a weak acid ($\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$), and CH_3COONa is a soluble salt that is completely dissociated in solution ($\text{CH}_3\text{COONa} \longrightarrow \text{Na}^+ + \text{CH}_3\text{COO}^-$). The common ion here is the acetate ion (CH_3COO^-). At equilibrium, the major species in solution are CH_3COOH , CH_3COO^- , Na^+ , H^+ , and H_2O . The Na^+ ion has no acid or base properties, and we ignore the ionization of water. Because K_a is an

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equilibrium constant, its value is the same whether we have just the acid or a mixture of the acid and its salt in solution. Therefore, we can calculate $[H^+]$ at equilibrium and hence pH if we know the equilibrium concentrations of both $[CH_3COOH]$ and $[CH_3COO^-]$. For CH_3COOH , K_a is 1.8×10^{-5} (see Table 11.3) giving a pK_a of 4.74. (b) For a solution of CH_3COOH , a weak acid, we calculate the $[H^+]$ at equilibrium, and hence the pH, using the initial concentration of CH_3COOH . This problem can be solved by following the same procedure as in Example 11.11.

Solution (a) Sodium acetate is a strong electrolyte, so it dissociates completely in solution:



The initial concentrations, changes, and final concentrations of the species involved in the equilibrium are

| | CH_3COOH | H^+ | CH_3COO^- |
|-----------------|------------|-------|-------------|
| Initial (M) | 0.20 | 0 | 0.30 |
| Change (M) | $-x$ | $+x$ | $+x$ |
| Equilibrium (M) | $0.20 - x$ | x | $0.30 + x$ |

Assuming that x is small, then $0.30 + x \approx 0.30$ and $0.20 - x \approx 0.20$. The Henderson-Hasselbalch equation (Equation 12.1) then gives

$$\begin{aligned} pH &= pK_a + \log_{10} \frac{[A^-]}{[HA]} \\ &= 4.74 + \log_{10} \frac{0.30}{0.20} \\ &= 4.92 \end{aligned}$$

The value of $x = [H^+]$ corresponding to this pH is between $10^{-4} M$ and $10^{-5} M$, which is significantly less than 5 percent of the initial concentrations of the acid or salt, so the approximation is valid.

(b) As in Example 11.11, $x = [H^+]$ is determined from

$$K_a = \frac{x^2}{[CH_3COOH]_0 - x}$$

Assuming that $x \ll [CH_3COOH]_0$ gives

$$\begin{aligned} x &= \sqrt{K_a[CH_3COOH]_0} = \sqrt{(1.8 \times 10^{-5})(0.20)} \\ &= 1.9 \times 10^{-3} \end{aligned}$$

Thus,

$$pH = -\log_{10} (1.9 \times 10^{-3}) = 2.72$$

In this case, x is less than 5 percent of the initial acid concentration, so the approximation is valid.

Check Comparing the results in parts (a) and (b), we see that when the common ion (CH_3COO^-) is present, according to Le Châtelier's principle, the equilibrium shifts from right to left. This action decreases the extent of ionization of the weak acid. Consequently, fewer H^+ ions are produced in (a) and the pH of the solution is

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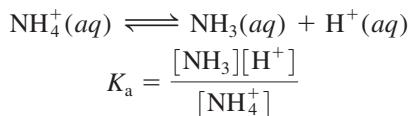
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higher than that in part (b). As always, you should check the validity of the assumptions.

Comment Note that, if the initial concentrations were small enough that the approximation used in part (a) were not valid, then the problem must be solved by substituting the concentrations $[CH_3COOH] = 0.20 - x$, $[CH_3COO^-] = 0.30 - x$, and $[H^+] = x$ into the expression for K_a and solving the resulting quadratic equation for x .

Practice Exercise What is the pH of a solution containing 0.30 M HCOOH and 0.52 M HCOOK?

The common ion effect also operates in a solution containing a weak base, such as NH_3 , and a salt of the base, say NH_4Cl . At equilibrium



We can derive the Henderson-Hasselbalch equation for this system as follows: Rearranging the preceding equation we obtain

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

Taking the negative logarithm of both sides gives

$$\begin{aligned} -\log_{10}[H^+] &= -\log_{10}K_a - \log_{10}\frac{[NH_4^+]}{[NH_3]} \\ -\log_{10}[H^+] &= -\log_{10}K_a + \log_{10}\frac{[NH_3]}{[NH_4^+]} \end{aligned}$$

or

$$pH = pK_a + \log_{10}\frac{[NH_3]}{[NH_4^+]}$$

A solution containing both NH_3 and its salt NH_4Cl is *less* basic than a solution containing only NH_3 at the same concentration. The common ion NH_4^+ suppresses the ionization of NH_3 in the solution containing both the base and the salt.



EACH 100 mL CONTAINS Dobutamine Hydrochloride USP EQUIVALENT TO 200 mg DOBUTAMINE 5-Demethyl-2-hydroxy-3-(2-hydroxyethyl)SODIUM BISULFATE ADDED AS A STABILIZER. pH ADJUSTED WITH SODIUM HYDROXIDE AND/OR HYDROCHLORIC ACID. pH 3.5 (2.5 to 5.5). OSMOLALITY 266 mOsmol/L (CALC.). STERILE. NONPYROGENIC. SINGLE DOSE CONTAINER. DRUG ADDITIVES SHOULD NOT BE MADE TO THIS SOLUTION. DOSAGE INTRAVENOUSLY AS DIRECTED BY A PHYSICIAN. SEE DIRECTIONS. CAUTIONS. MUST NOT BE USED IN

12.2 | The pH of a Buffer Solution Is Resistant to Large Changes in pH

A **buffer solution** is a solution of (1) a weak acid or a weak base and (2) its salt; both components must be present. The solution has the ability to resist changes in pH upon the addition of small amounts of either acid or base. Buffers are very important to chemical and biological systems. The pH in the human body varies greatly from one fluid to another; for example, the pH of blood is about 7.4, whereas the gastric juice in our stomachs has a pH of about 1.5. These pH values, which are crucial for

Fluids for intravenous injection must include buffer systems to maintain the proper blood pH.

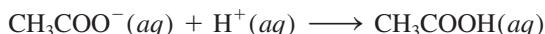
proper enzyme function and the balance of osmotic pressure, are maintained by buffers in most cases.

A buffer solution must contain a relatively large concentration of acid to react with any OH^- ions that are added to it, and it must contain a similar concentration of base to react with any added H^+ ions. Furthermore, the acid and the base components of the buffer must not consume each other in a neutralization reaction. These requirements are satisfied by an acid-base conjugate pair, for example, a weak acid and its conjugate base (supplied by a salt) or a weak base and its conjugate acid (supplied by a salt).

A simple buffer solution can be prepared by adding comparable molar amounts of acetic acid (CH_3COOH) and its salt sodium acetate (CH_3COONa) to water. The equilibrium concentrations of both the acid and the conjugate base (from CH_3COONa) can generally be assumed to be the same as the starting concentrations because both the acid (CH_3COOH) and its conjugate base (CH_3COO^-) are weak electrolytes. A solution containing these two substances has the ability to neutralize either added acid or added base. Sodium acetate, a strong electrolyte, dissociates completely in water:



If an acid is added, the H^+ ions will be neutralized by the conjugate base in the buffer (CH_3COO^-) according to the equation



If a base is added to the buffer system, the OH^- ions will be neutralized by the acid in the buffer:

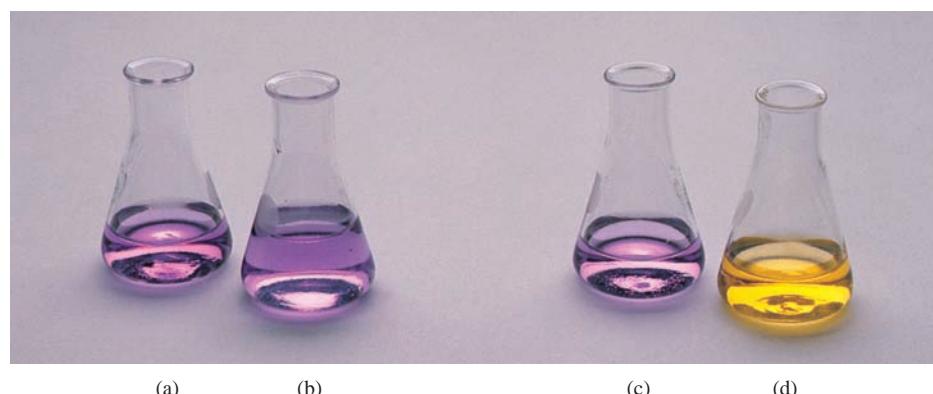


As you can see, the two reactions that characterize this buffer system are identical to those for the common ion effect described in Example 12.1. The *buffering capacity*, that is, the effectiveness of the buffer solution, depends on the amount of acid and conjugate base from which the buffer is made. The larger the amount, the greater the buffering capacity.

In general, a buffer system can be represented as salt-acid or conjugate base-acid. Thus, the sodium acetate-acetic acid buffer system discussed previously can be written as $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ or simply $\text{CH}_3\text{COO}^-/\text{CH}_3\text{COOH}$. Figure 12.1 shows this buffer system in action.

Example 12.2 distinguishes buffer systems from acid-salt combinations that do not function as buffers.

Figure 12.1 The acid-base indicator bromophenol blue (added to all solutions shown) is used to illustrate buffer action. The color of the indicator is blue-purple above pH = 4.6 and yellow below pH = 3.0. (a) A buffer solution made up of 50 mL of 0.1 M CH_3COOH and 50 mL of 0.1 M CH_3COONa . The solution has a pH of 4.7 and turns the indicator blue-purple. (b) After the addition of 40 mL of 0.1 M HCl solution to the solution in part (a), the color remains blue-purple. (c) A 100-mL CH_3COOH solution whose pH is 4.7. (d) After the addition of 6 drops (about 0.3 mL) of 0.1 M HCl solution, the color turns yellow. Without buffer action, the pH of the solution decreases rapidly to less than 3.0 upon the addition of 0.1 M HCl.



Example 12.2

Which of the following solutions can be classified as buffer systems: (a) $\text{KH}_2\text{PO}_4/\text{H}_3\text{PO}_4$, (b) $\text{NaClO}_4/\text{HClO}_4$, and (c) $\text{C}_5\text{H}_5\text{N}/\text{C}_5\text{H}_5\text{NHCl}$ ($\text{C}_5\text{H}_5\text{N}$ is pyridine; its K_b is given in Table 11.4)? Explain your answer.

Strategy What constitutes a buffer system? Which of the preceding solutions contains a weak acid and its salt (containing the weak conjugate base)? Which of the preceding solutions contains a weak base and its salt (containing the weak conjugate acid)? Why is the conjugate base of a strong acid not able to neutralize an added acid?

Solution The criteria for a buffer system are that we must have a weak acid and its salt (containing the weak conjugate base) or a weak base and its salt (containing the weak conjugate acid).

- (a) H_3PO_4 is a weak acid, and its conjugate base, H_2PO_4^- , is a weak base (see Table 11.6). Therefore, this is a buffer system.
- (b) Because HClO_4 is a strong acid, its conjugate base, ClO_4^- , is an extremely weak base. This means that the ClO_4^- ion will not combine with an H^+ ion in solution to form HClO_4 . Thus, the system cannot act as a buffer system.
- (c) As Table 11.4 shows, $\text{C}_5\text{H}_5\text{N}$ is a weak base and its conjugate acid, $\text{C}_5\text{H}_5\text{NH}^+$ (the cation of the salt $\text{C}_5\text{H}_5\text{NHCl}$), is a weak acid. Therefore, this is a buffer system.

Practice Exercise Which of the following are buffer systems: (a) KF/HF , (b) KBr/HBr , and (c) $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$?

The pH of a buffer solution is governed by the Henderson-Hasselbalch equation (Equation 12.2)

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{conjugate base}]}{[\text{acid}]}$$

The form of this equation helps us understand the stability of a buffer solution to changes in pH from a mathematical perspective. In Equation 12.2, the logarithmic dependence of the pH on the ratio of conjugate base to acid means that in order for the pH to change by 1, the ratio of [conjugate base]/[acid] has to change by a factor of 10.

The effect of a buffer solution on pH is illustrated by Example 12.3.

Example 12.3

- (a) Calculate the pH of a buffer system containing 1.0 M CH_3COOH and 1.0 M CH_3COONa . (b) What is the pH of the buffer system after the addition of 0.10 mole of gaseous HCl to 1.0 L of the solution? Assume that the volume of the solution does not change when the HCl is added.

Strategy The pH of the buffer system before and after the addition of HCl can be calculated from the Henderson-Hasselbalch equation. The K_a of CH_3COOH is 1.8×10^{-5} (see Table 11.3) which gives a $\text{p}K_a$ of 4.74.

Solution (a) Both the weak acid (CH_3COOH) and its conjugate base (CH_3COO^- from CH_3COONa) are weak electrolytes and will not dissociate appreciably
 $[\text{CH}_3\text{COOH}] \approx [\text{CH}_3\text{COOH}]_0 = 1.0 \text{ M}$ and $[\text{CH}_3\text{COO}^-] \approx [\text{CH}_3\text{COO}^-]_0 = 1.0 \text{ M}$.

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(We must check this approximation at the end of the calculation.) The Henderson-Hasselbalch equation (Equation 12.2) gives

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log_{10} \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \\ &= 4.74 + \log_{10} \frac{1.0}{1.0} \\ &= 4.74 \end{aligned}$$

When the concentrations of the acid and its conjugate base are the same, the pH of the buffer is equal to the $\text{p}K_a$.

This corresponds to an H^+ ion concentration of between $10^{-4} M$ and $10^{-5} M$, so the approximation is valid.¹

- (b) When HCl (a strong acid) is added to the solution, it completely dissociates into H^+ ions and Cl^- ions. The initial changes are

| $\text{HCl}(aq) \longrightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$ | | | |
|---|-------|------|------|
| Initial (M) | 0.10 | 0.0 | 0.0 |
| Change (M) | -0.10 | 0.10 | 0.10 |
| Final (M) | 0.00 | 0.10 | 0.10 |

The H^+ ions are neutralized by the conjugate base (CH_3COO^-), and Cl^- is a spectator ion in solution because it is the conjugate base of a strong acid and will have no tendency to neutralize the weak acid present. At this point, it is more convenient to work with moles rather than molarity. The reason is that in some cases the volume of the solution may change when a substance is added. A change in volume will change the molarity, but not the number of moles. The neutralization reaction is summarized next:

| $\text{CH}_3\text{COO}^-(aq) + \text{H}^+(aq) \longrightarrow \text{CH}_3\text{COOH}(aq)$ | | | |
|---|-------|-------|-------|
| Initial (mol) | 1.0 | 0.10 | 1.0 |
| Change (mol) | -0.10 | -0.10 | +0.10 |
| Final (mol) | 0.90 | 0.00 | 1.10 |

Finally, to calculate the pH of the buffer after neutralization of the acid, we convert back to molarity by dividing moles by 1.0 L of solution. Thus, the weak acid concentration, $[\text{CH}_3\text{COOH}]$ after addition of HCl is $1.10 M$ and the conjugate base concentration $[\text{CH}_3\text{COO}^-] = 0.90 M$. Reapplying the Henderson-Hasselbalch equation gives

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log_{10} \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \\ &= 4.74 + \log_{10} \frac{0.90}{1.10} \\ &= 4.65 \end{aligned}$$

Practice Exercise Calculate the pH of the $0.30 M \text{ NH}_3/0.36 M \text{ NH}_4\text{Cl}$ buffer system. What is the pH after the addition of 20.0 mL of $0.050 M \text{ NaOH}$ to 80.0 mL of the buffer solution?

1. Although the approximation that the dissociation is small is valid, the results here will only be approximate because of the high concentrations of solute ($\sim 1 M$). At such concentrations, the interactions among solute ions and molecules will be strong, and the solute activities will deviate somewhat from their concentrations. See the discussion in Section 10.1.

In the buffer solution examined in Example 12.3, there is a decrease in pH (the solution becomes more acidic) as a result of the added HCl. We can also compare the changes in H^+ ion concentration as follows

$$\begin{aligned}\text{before addition of HCl: } [\text{H}^+] &= 10^{-4.74} = 1.8 \times 10^{-5} \text{ M} \\ \text{after addition of HCl: } [\text{H}^+] &= 10^{-4.65} = 2.2 \times 10^{-5} \text{ M}\end{aligned}$$

Thus, the H^+ ion concentration increases by a factor of

$$\frac{2.2 \times 10^{-5}}{1.8 \times 10^{-5}} = 1.2$$

To appreciate the effectiveness of the $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ buffer, let us find out what would happen if 0.10 mol HCl were added to 1.0 L of pure water ($\text{pH} = 7$), and compare the increase in H^+ ion concentration.

$$\begin{aligned}\text{before addition of HCl: } [\text{H}^+] &= 1.0 \times 10^{-7} \text{ M} \\ \text{after addition of HCl: } [\text{H}^+] &= 0.10 \text{ M}\end{aligned}$$

As a result of the addition of HCl, the H^+ ion concentration increases by a factor of 10^6 , amounting to a million-fold increase! This comparison shows that a properly chosen buffer solution can maintain a fairly constant H^+ ion concentration, or pH (Figure 12.2).

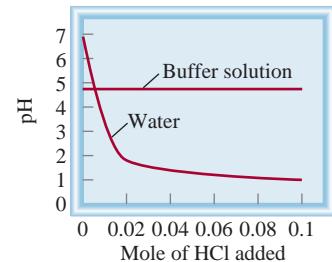


Figure 12.2 A comparison of the change in pH when 0.10 mol HCl is added to 1 L of pure water and to 1 L of an acetate buffer solution, as described in Example 12.3.

Preparing a Buffer Solution with a Specific pH

Now suppose we want to prepare a buffer solution with a specific pH. How do we go about it? Equation 12.2 indicates that if the molar concentrations of the acid and its conjugate base are approximately equal, that is, if $[\text{acid}] \approx [\text{conjugate base}]$, then

$$\log_{10} \frac{[\text{conjugate base}]}{[\text{acid}]} \approx 0$$

$$\text{pH} \approx \text{p}K_a$$

Thus, to prepare a buffer solution, we work backward. First we choose a weak acid whose $\text{p}K_a$ is close to the desired pH. Next, we substitute the pH and $\text{p}K_a$ values in Equation 12.2 to obtain the ratio $[\text{conjugate base}]/[\text{acid}]$. This ratio can then be converted to molar quantities for the preparation of the buffer solution. Example 12.4 shows this approach.

Example 12.4

Describe how you would prepare a “phosphate buffer” with a pH of about 7.40.

Strategy For a buffer to function effectively, the concentrations of the acid component must be roughly equal to the conjugate base component. According to Equation 12.2, when the desired pH is close to the $\text{p}K_a$ of the acid, $\text{pH} \approx \text{p}K_a$,

$$\log_{10} \frac{[\text{conjugate base}]}{[\text{acid}]} \approx 0$$

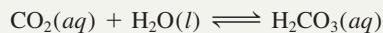
$$\frac{[\text{conjugate base}]}{[\text{acid}]} \approx 1$$

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Maintaining the pH of Blood

All higher animals need a circulatory system to carry fuel and oxygen for their life processes and to remove wastes. In the human body, this vital exchange takes place in the versatile fluid known as blood, of which there are about 5 L in an average adult. Blood circulating deep in the tissues carries oxygen and nutrients to keep cells alive, and removes carbon dioxide and other waste materials. Using several buffer systems, nature has provided an extremely efficient method for the delivery of oxygen and the removal of carbon dioxide.

Blood is an enormously complex system, but for our purposes we need look at only two essential components: blood plasma and red blood cells, or *erythrocytes*. Blood plasma contains many compounds, including proteins, metal ions, and inorganic phosphates. The erythrocytes contain hemoglobin molecules, as well as the enzyme *carbonic anhydrase*, which catalyzes both the formation of carbonic acid (H_2CO_3) and its decomposition:



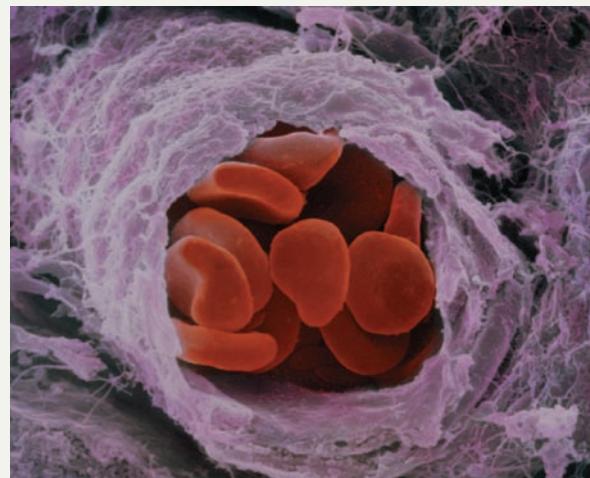
The substances inside the erythrocyte are protected from extracellular fluid (blood plasma) by a cell membrane that allows only certain molecules to diffuse through it. The pH of blood plasma is maintained at about 7.40 by several buffer systems, the most important of which is the $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ system. In the erythrocyte, where the pH is 7.25, the principal buffer systems are $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ and hemoglobin. The hemoglobin molecule is a complex protein molecule (molar mass 65,000 g) that contains a number of ionizable protons. As a very rough approximation, we can treat it as a monoprotic acid of the form HHb:



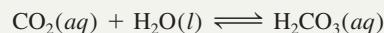
where HHb represents the hemoglobin molecule and Hb^- the conjugate base of HHb. Oxyhemoglobin (HHbO_2), formed by the combination of oxygen with hemoglobin, is a stronger acid than HHb:



As the figure on page 621 shows, carbon dioxide produced by metabolic processes diffuses into the erythrocyte, where it is rapidly converted to H_2CO_3 by carbonic anhydrase:



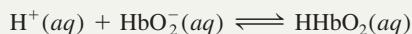
Electron micrograph of red blood cells in a small branch of an artery (color added).



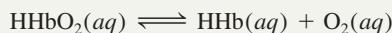
The ionization of the carbonic acid



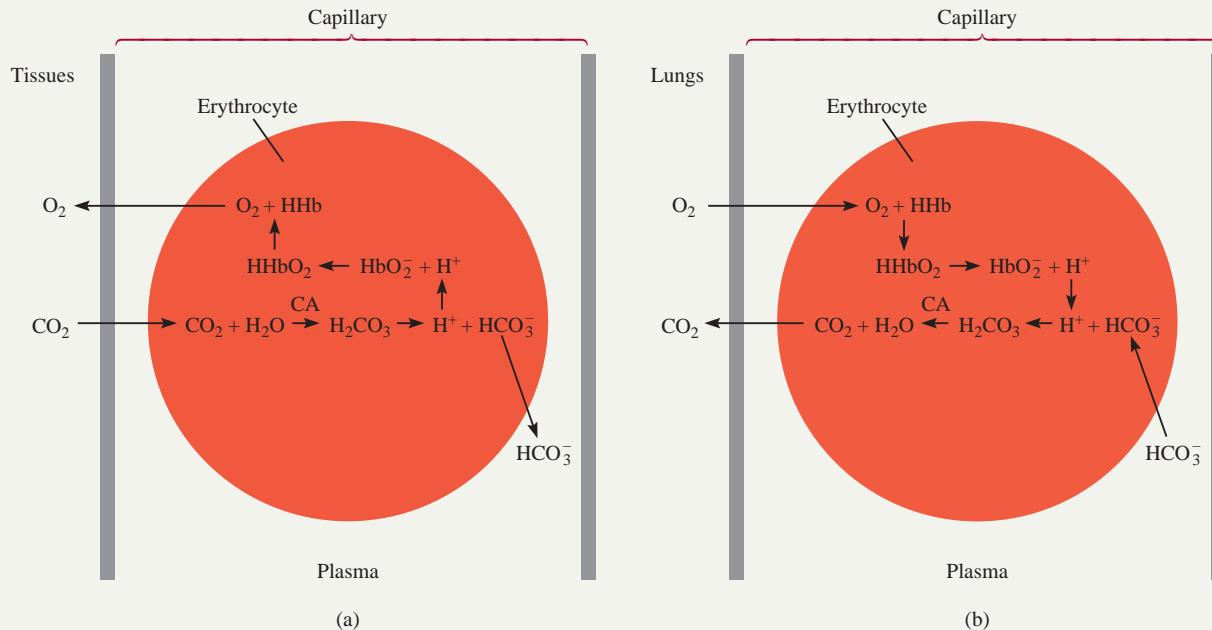
has two important consequences. First, the bicarbonate ion diffuses out of the erythrocyte and is carried by the blood plasma to the lungs. This is the major mechanism for removing carbon dioxide. Second, the H^+ ions shift the equilibrium in favor of the nonionized oxyhemoglobin molecule:



Because HHbO_2 releases oxygen more readily than does its conjugate base (HbO_2^-), the formation of the acid promotes the following reaction from left to right:



The O_2 molecules diffuse out of the erythrocyte and are taken up by other cells to carry out metabolism. When the venous blood returns to the lungs, the preceding processes are reversed. The bicarbonate ions now diffuse into the

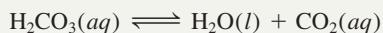


Oxygen–carbon dioxide transport and release by blood. (a) The partial pressure of CO_2 is higher in the metabolizing tissues than in the plasma. Thus, it diffuses into the blood capillaries and then into erythrocytes. There it is converted to carbonic acid by the enzyme carbonic anhydrase (CA). The protons provided by the carbonic acid then combine with the HbO_2^- anions to form $HHbO_2$, which eventually dissociates into HHb and O_2 . Because the partial pressure of O_2 is higher in the erythrocytes than in the tissues, oxygen molecules diffuse out of the erythrocytes and then into the tissues. The bicarbonate ions also diffuse out of the erythrocytes and are carried by the plasma to the lungs. (b) In the lungs, the processes are exactly reversed. Oxygen molecules diffuse from the lungs, where they have a higher partial pressure, into the erythrocytes. There they combine with HHb to form $HHbO_2$. The protons provided by $HHbO_2$ combine with the bicarbonate ions diffused into the erythrocytes from the plasma to form carbonic acid. In the presence of carbonic anhydrase, carbonic acid is converted to H_2O and CO_2 . The CO_2 then diffuses out of the erythrocytes and into the lungs, where it is exhaled.

erythrocyte, where they react with hemoglobin to form carbonic acid:

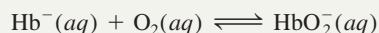


Most of the acid is then converted to CO_2 by carbonic anhydrase:



The carbon dioxide diffuses to the lungs and is eventually exhaled. The formation of the Hb^- ions (due to the reaction

between HHb and HCO_3^-) also favors the uptake of oxygen at the lungs

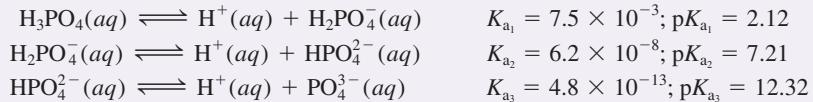


because Hb^- has a greater affinity for oxygen than does HHb .

When the arterial blood flows back to the body tissues, the entire cycle is repeated.

Continued—

Solution Because phosphoric acid is a triprotic acid, we write the three stages of ionization as follows. The K_a and pK_a values are obtained from Table 11.6, and the pK_a values are obtained by applying Equation 11.15



The most suitable of the three buffer systems is $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$ because the pK_a of the acid H_2PO_4^- is closest to the desired pH. From the Henderson-Hasselbalch equation (Equation 12.2), we write

$$\begin{aligned} \text{pH} &= pK_a + \log_{10} \frac{[\text{conjugate base}]}{[\text{acid}]} \\ 7.40 &= 7.21 + \log_{10} \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \\ \log_{10} \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} &= 0.19 \end{aligned}$$

Taking the antilog, we obtain

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 10^{0.19} = 1.5$$

Thus, one way to prepare a phosphate buffer with a pH of 7.40 is to dissolve disodium hydrogen phosphate (Na_2HPO_4) and sodium dihydrogen phosphate (NaH_2PO_4) in a mole ratio of 1.5:1.0 in water. For example, we could dissolve 1.5 moles of Na_2HPO_4 and 1.0 mole of NaH_2PO_4 in enough water to make up a 1-L solution.

Practice Exercise How would you prepare a liter of “carbonate buffer” at a pH of 10.10? You are provided with carbonic acid (H_2CO_3), sodium hydrogen carbonate (NaHCO_3), and sodium carbonate (Na_2CO_3). See Table 11.6 for K_a values.

12.3 | The Concentration of an Unknown Acid or Base Can Be Determined by Titration

Quantitative studies of acid-base neutralization reactions are most conveniently carried out using a technique known as titration. In a *titration*, a solution of accurately known concentration, called a *standard solution*, is added gradually to another solution of unknown concentration, until the chemical reaction between the two solutions is complete. If we know the volumes of the standard and unknown solutions used in the titration, along with the concentration of the standard solution, we can calculate the concentration of the unknown solution.

Sodium hydroxide is one of the bases commonly used in the laboratory. However, it is difficult to obtain solid sodium hydroxide in a pure form because it has a tendency to absorb water from air, and its solution reacts with carbon dioxide. For these reasons, a solution of sodium hydroxide must be *standardized* before it can be used in accurate analytical work. We can standardize the sodium hydroxide solution by titrating it against an acid solution of accurately known concentration. The acid often chosen for this task is a weak acid called potassium hydrogen phthalate (KHP), for which the

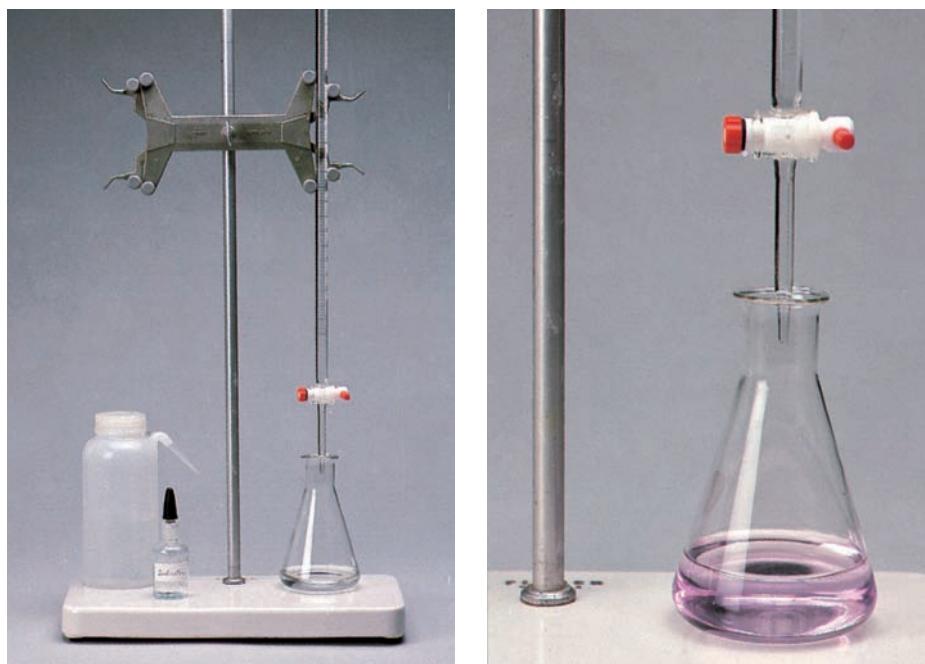
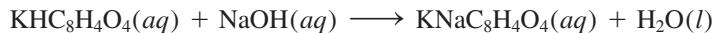


Figure 12.3 (a) Apparatus for an acid-base titration. An NaOH solution is added from the buret to a KHP solution in an Erlenmeyer flask. (b) A reddish-pink color appears when the equivalence point is reached. The color here has been intensified for visual display.

molecular formula is $\text{KHC}_8\text{H}_4\text{O}_4$. KHP is a white, soluble solid that is commercially available in highly pure form. The reaction between KHP and sodium hydroxide is



and the net ionic equation is



The apparatus for the titration is shown in Figure 12.3. First, a known amount of KHP is transferred to an Erlenmeyer flask, and some distilled water is added to make up a solution. Next, an NaOH solution is carefully added to the KHP solution from a buret until we reach the **equivalence point**, that is, *the point at which the acid has completely reacted with or been neutralized by the base*. The equivalence point is usually signaled by a sharp change in the color of an indicator in the acid solution. In acid-base titrations, *indicators* are substances that have distinctly different colors in acidic and basic media. One commonly used indicator is phenolphthalein, which is colorless in acidic and neutral solutions but reddish pink in basic solutions. Indicators will be discussed in more detail in Section 12.4. At the equivalence point, all the KHP present has been neutralized by the added NaOH and the solution is still colorless. However, if we add just one more drop of NaOH solution from the buret, the solution will immediately turn pink because the solution is now basic.

Having discussed buffer solutions, we can now look in more detail at the quantitative aspects of acid-base titrations. We will consider three types of reactions: (1) titrations involving a strong acid and a strong base, (2) titrations involving a weak acid and a strong base, and (3) titrations involving a strong acid and a weak base. Titrations involving a weak acid and a weak base are complicated by the hydrolysis of both the cation and the anion of the salt formed. These titrations will not be dealt with in this text. Figure 12.4 shows the arrangement for monitoring the pH during the course of a titration.

Figure 12.4 A pH meter is used to monitor an acid-base titration.

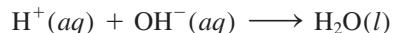


Strong Acid–Strong Base Titrations

The reaction between a strong acid (say, HCl) and a strong base (say, NaOH) can be represented by



or in terms of the net ionic equation



Consider the addition of a 0.100 M NaOH solution (from a buret) to an Erlenmeyer flask containing 25.0 mL of 0.100 M HCl. Figure 12.5 shows the pH profile of the titration (also known as the *titration curve*). Before the addition of NaOH, the pH of the acid is given (approximately) by $-\log(0.100)$, or 1.00. When NaOH is added, the pH of the

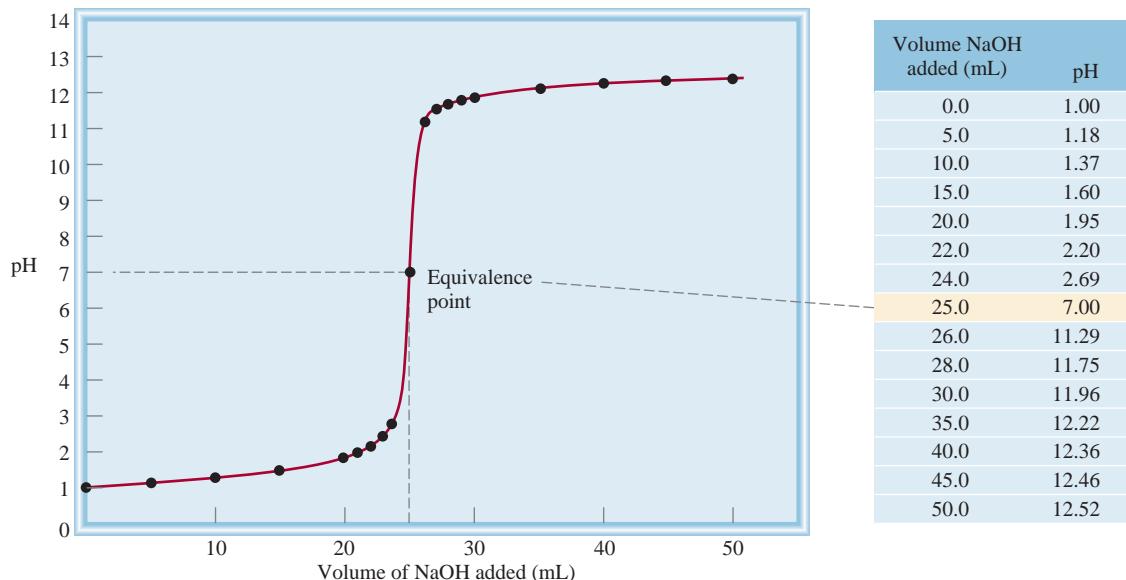


Figure 12.5 The pH profile for the titration of a strong acid with a strong base. A 0.100 M NaOH solution is added from a buret to 25.0 mL of a 0.100 M HCl solution in an Erlenmeyer flask (see Figure 12.3). This curve is sometimes referred to as a titration curve.

solution increases slowly at first. Near the equivalence point, the pH begins to rise steeply, and at the equivalence point (that is, the point at which equimolar amounts of acid and base have reacted) the curve rises almost vertically. In a strong acid-strong base titration, both the hydrogen ion and hydroxide ion concentrations are very small at the equivalence point (approximately $1 \times 10^{-7} M$); consequently, the addition of a single drop of the base can cause a large increase in $[OH^-]$ and in the pH of the solution. Beyond the equivalence point, the pH again increases slowly with the addition of NaOH.

It is possible to calculate the pH of the solution at every stage of titration. Here are three sample calculations.

1. After the addition of 10.0 mL of 0.100 M NaOH to 25.0 mL of 0.100 M HCl. The total volume of the solution is 35.0 mL. The number of moles of NaOH in 10.0 mL is

$$10.0 \text{ mL} \times \frac{0.100 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 1.00 \times 10^{-3} \text{ mol}$$

The number of moles of HCl originally present in 25.0 mL of solution is

$$25.0 \text{ mL} \times \frac{0.100 \text{ mol HCl}}{1 \text{ L HCl}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2.50 \times 10^{-3} \text{ mol}$$

Thus, the amount of HCl left after partial neutralization is $(2.50 \times 10^{-3}) - (1.00 \times 10^{-3})$, or 1.50×10^{-3} mol. Next, the concentration of H^+ ions in 35.0 mL of solution is found as follows:

$$\frac{1.50 \times 10^{-3} \text{ mol HCl}}{35.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.0429 \text{ mol L}^{-1} = 0.0429 M$$

Thus, $[H^+] = 0.0429 M$, and the pH of the solution is

$$pH \approx -\log_{10} 0.0429 = 1.37$$

2. After the addition of 25.0 mL of 0.100 M NaOH to 25.0 mL of 0.100 M HCl.

This is a simple calculation, because it involves a complete neutralization reaction and the salt (NaCl) does not undergo hydrolysis. At the equivalence point,

$$[H^+] = [OH^-] = 1.00 \times 10^{-7} M$$

Neither Na^+ nor Cl^- undergoes hydrolysis.

and the pH of the solution is 7.00.

3. After the addition of 35.0 mL of 0.100 M NaOH to 25.0 mL of 0.100 M HCl. The total volume of the solution is now 60.0 mL. The number of moles of NaOH added is

$$35.0 \text{ mL} \times \frac{0.100 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 3.50 \times 10^{-3} \text{ mol}$$

The number of moles of HCl in 25.0 mL solution is 2.50×10^{-3} mol. After complete neutralization of HCl, the number of moles of NaOH left is $(3.50 \times 10^{-3}) - (2.50 \times 10^{-3})$, or 1.00×10^{-3} mol. The concentration of OH^- in 60.0 mL of solution is

$$\frac{1.00 \times 10^{-3} \text{ mol } OH^-}{60.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.0167 \text{ mol L}^{-1} = 0.0167 M$$

Thus, $[\text{OH}^-] = 0.0167 \text{ M}$ and $\text{pOH} = -\log_{10} 0.0167 = 1.78$. Hence, the pH of the solution is

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.78 = 12.22$$

Weak Acid–Strong Base Titrations

Consider the neutralization reaction between acetic acid (a weak acid) and sodium hydroxide (a strong base):



This equation can be simplified to



The acetate ion undergoes hydrolysis as follows:



Therefore, at the equivalence point, when we only have sodium acetate present, the pH will be *greater than 7* as a result of the excess OH^- ions formed (Figure 12.6). Note that this situation is analogous to the hydrolysis of sodium acetate (CH_3COONa) (see page 594).

Example 12.5 deals with the titration of a weak acid with a strong base.

Example 12.5

Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid by sodium hydroxide after the addition to the acid solution of (a) 10.0 mL of 0.100 M NaOH, (b) 25.0 mL of 0.100 M NaOH, or (c) 35.0 mL of 0.100 M NaOH.

—Continued

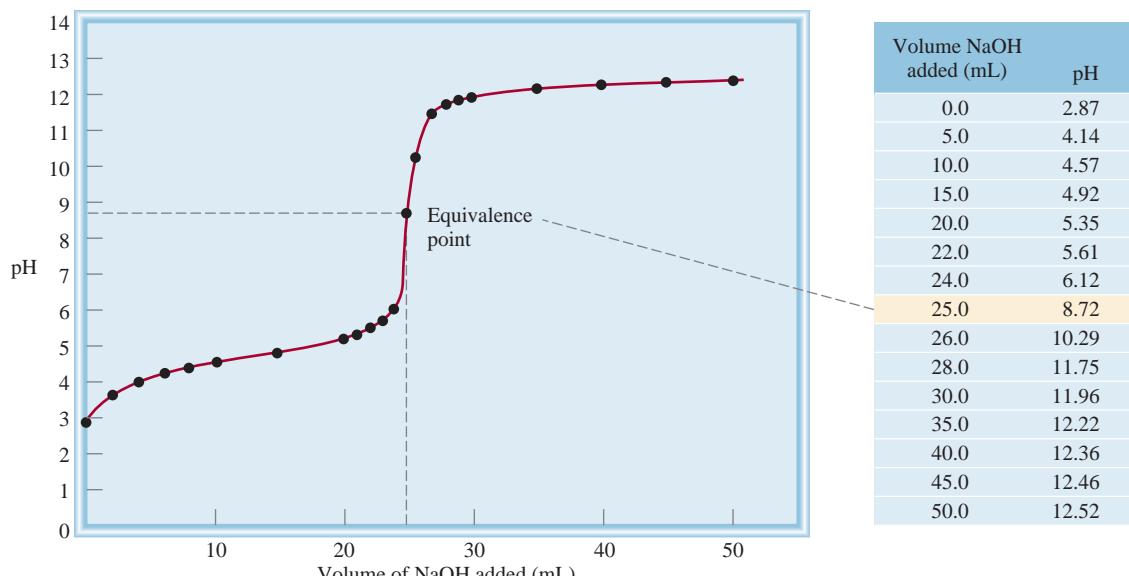


Figure 12.6 The pH profile of a weak acid–strong base titration. A 0.100 M NaOH solution is added from a buret to 25.0 mL of a 0.100 M CH_3COOH solution in an Erlenmeyer flask. Because of the hydrolysis of the salt formed, the pH at the equivalence point is greater than 7.

Continued—

Strategy The reaction between CH₃COOH and NaOH is



We see that 1 mol CH₃COOH ≈ 1 mol NaOH. Therefore, at every stage of the titration, we can calculate the number of moles of base reacting with the acid, and the pH of the solution is determined by the excess acid or base left over. At the equivalence point, however, the neutralization is complete, and the pH of the solution will depend on the extent of the hydrolysis of the salt formed, which is CH₃COONa.

Solution (a) The number of moles of NaOH in 10.0 mL is

$$10.0 \text{ mL} \times \frac{0.100 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 1.00 \times 10^{-3} \text{ mol}$$

The number of moles of CH₃COOH originally present in 25.0 mL of solution is

$$25.0 \text{ mL} \times \frac{0.100 \text{ mol CH}_3\text{COOH}}{1 \text{ L CH}_3\text{COOH}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2.50 \times 10^{-3} \text{ mol}$$

We work with moles at this point because when two solutions are mixed, the solution volume increases. As the volume increases, molarity will change, but the number of moles will remain the same. The changes in the number of moles are summarized next:

| $\text{CH}_3\text{COOH}(aq) + \text{NaOH}(aq) \longrightarrow \text{CH}_3\text{COONa}(aq) + \text{H}_2\text{O}(l)$ | | | |
|--|------------------------|------------------------|------------------------|
| Initial (mol) | 2.50×10^{-3} | 1.00×10^{-3} | 0 |
| Change (mol) | -1.00×10^{-3} | -1.00×10^{-3} | $+1.00 \times 10^{-3}$ |
| Final (mol) | 1.50×10^{-3} | 0 | 1.00×10^{-3} |

At this stage, we have a buffer system made up of CH₃COOH and CH₃COO[−] (from the salt, CH₃COONa). To calculate the pH of the solution, we can use the Henderson-Hasselbalch equation (Equation 12.2):

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log_{10} \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \\ &= 4.74 + \log_{10} \frac{1.00 \times 10^{-3}}{1.50 \times 10^{-3}} \\ &= 4.74 - 0.18 \\ &= 4.56 \end{aligned}$$

Because the volume of the solution is the same for CH₃COOH and CH₃COO[−] (35 mL), the ratio of the number of moles present is equal to the ratio of their molar concentrations.

(b) These quantities (that is, 25.0 mL of 0.100 M NaOH reacting with 25.0 mL of 0.100 M CH₃COOH) correspond to the equivalence point. The number of moles of NaOH in 25.0 mL of the solution is

$$25.0 \text{ mL} \times \frac{0.100 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2.50 \times 10^{-3} \text{ mol}$$

The changes in number of moles are summarized next:

| $\text{CH}_3\text{COOH}(aq) + \text{NaOH}(aq) \longrightarrow \text{CH}_3\text{COONa}(aq) + \text{H}_2\text{O}(l)$ | | | |
|--|------------------------|------------------------|------------------------|
| Initial (mol) | 2.50×10^{-3} | 2.50×10^{-3} | 0 |
| Change (mol) | -2.50×10^{-3} | -2.50×10^{-3} | $+2.50 \times 10^{-3}$ |
| Final (mol) | 0 | 0 | 2.50×10^{-3} |

—Continued

Continued—

At the equivalence point, the concentrations of both the acid and the base are zero. The total volume is $(25.0 + 25.0)$ mL or 50.0 mL, so the concentration of the salt is

$$\begin{aligned} [\text{CH}_3\text{COONa}] &= \frac{2.50 \times 10^{-3} \text{ mol}}{50.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \\ &= 0.0500 \text{ mol L}^{-1} = 0.0500 \text{ M} \end{aligned}$$

The next step is to calculate the pH of the solution that results from the hydrolysis of the CH_3COO^- ions:



Following the procedure described in Example 11.17 and looking up the base ionization constant (K_b) for CH_3COO^- in Table 11.5, we write

$$\begin{aligned} K_b &= 5.6 \times 10^{-10} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{x^2}{0.0500 - x} \\ x &= [\text{OH}^-] = 5.3 \times 10^{-6} \text{ M}, \text{ pH} = 8.72 \end{aligned}$$

- (c) After the addition of 35.0 mL of NaOH, the solution is well past the equivalence point. The number of moles of NaOH originally present is

$$35.0 \text{ mL} \times \frac{0.100 \text{ mol NaOH}}{1 \text{ L NaOH}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 3.50 \times 10^{-3} \text{ mol}$$

The changes in number of moles are summarized next:

| $\text{CH}_3\text{COOH}(aq) + \text{NaOH}(aq) \longrightarrow \text{CH}_3\text{COONa}(aq) + \text{H}_2\text{O}(l)$ | | | |
|--|------------------------|------------------------|------------------------|
| Initial (mol) | 2.50×10^{-3} | 3.50×10^{-3} | 0 |
| Change (mol) | -2.50×10^{-3} | -2.50×10^{-3} | $+2.50 \times 10^{-3}$ |
| Final (mol) | 0 | 1.00×10^{-3} | 2.50×10^{-3} |

At this stage, we have two species in solution that are responsible for making the solution basic: OH^- and CH_3COO^- (from CH_3COONa). However, because OH^- is a much stronger base than CH_3COO^- , we can safely neglect the hydrolysis of the CH_3COO^- ions and calculate the pH of the solution using only the concentration of the OH^- ions. The total volume of the combined solutions is $(25.0 + 35.0)$ mL or 60.0 mL, so we calculate OH^- concentration as follows:

$$[\text{OH}^-] = \frac{1.00 \times 10^{-3} \text{ mol}}{60.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.0167 \text{ mol L}^{-1} = 0.0167 \text{ M}$$

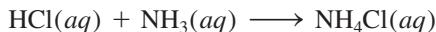
$$\text{pOH} = -\log_{10} [\text{OH}^-] = -\log_{10} 0.0167 = 1.78$$

$$\text{pH} = 14.00 - 1.78 = 12.22$$

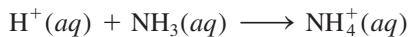
Practice Exercise Exactly 100 mL of 0.10 M nitrous acid (HNO_2) is titrated with a 0.10 M NaOH solution. Calculate the pH for (a) the initial solution, (b) the point at which 80 mL of the base has been added, (c) the equivalence point, and (d) the point at which 105 mL of the base has been added.

Strong Acid–Weak Base Titrations

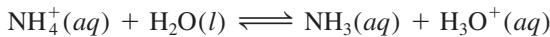
Consider the titration of HCl, a strong acid, with NH₃, a weak base:



or simply



The pH at the equivalence point is *less than* 7 due to the hydrolysis of the NH₄⁺ ion:



or simply

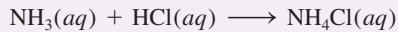


Because of the volatility of an aqueous ammonia solution, it is more convenient to add hydrochloric acid from a buret to the ammonia solution. Figure 12.7 shows the titration curve for this experiment.

Example 12.6

Calculate the pH at the equivalence point when 25.0 mL of 0.100 M NH₃ is titrated by a 0.100 M HCl solution.

Strategy The reaction between NH₃ and HCl is



—Continued

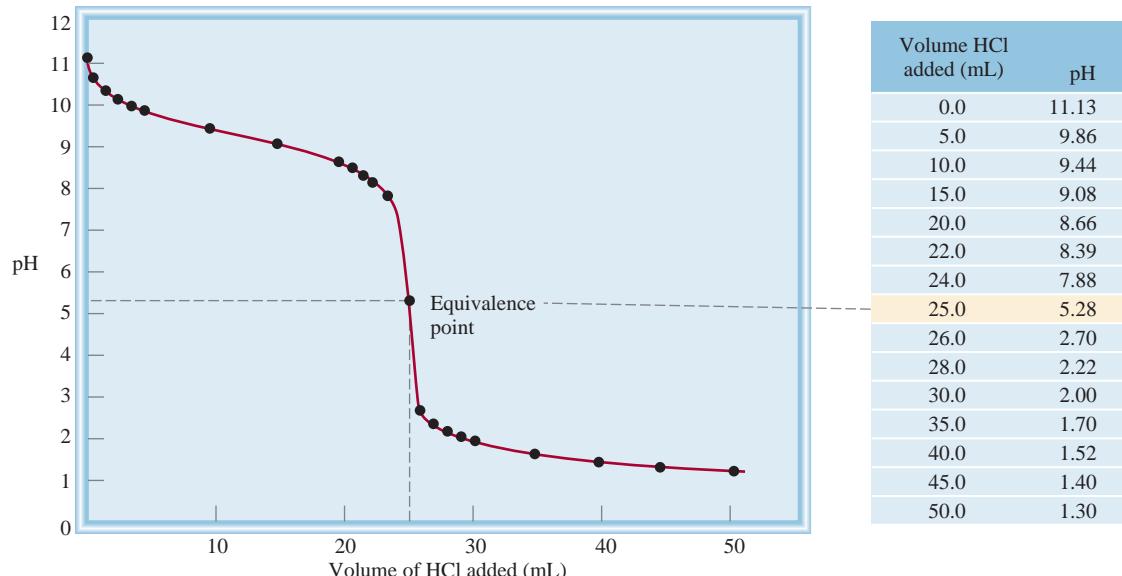


Figure 12.7 The pH profile for the titration of a weak base with a strong acid. A 0.100 M HCl solution is added from a buret to 25.0 mL of a 0.100 M NH₃ solution in an Erlenmeyer flask. Because of the hydrolysis of the salt formed, the pH at the equivalence point is less than 7.

Continued—

We see that 1 mol $\text{NH}_3 \approx 1$ mol HCl. At the equivalence point, the major species in solution are the salt NH_4Cl (dissociated into NH_4^+ and Cl^- ions) and H_2O . First we determine the concentration of NH_4Cl formed. Then we calculate the pH as a result of the NH_4^+ ion hydrolysis. The Cl^- ion, being the conjugate base of a strong acid HCl, does not react with water. As usual, we ignore the ionization of water.

Solution The number of moles of NH_3 in 25.0 mL of 0.100 M solution is

$$25.0 \text{ mL} \times \frac{0.100 \text{ mol } \text{NH}_3}{1 \text{ L } \text{NH}_3} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2.50 \times 10^{-3} \text{ mol}$$

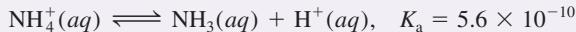
At the equivalence point, the number of moles of HCl added equals the number of moles of NH_3 . The changes in the number of moles are summarized here:

| | $\text{NH}_3(aq)$ | + | $\text{HCl}(aq)$ | \longrightarrow | $\text{NH}_4\text{Cl}(aq)$ |
|---------------|------------------------|---|------------------------|-------------------|----------------------------|
| Initial (mol) | 2.50×10^{-3} | | 2.50×10^{-3} | | 0 |
| Change (mol) | -2.50×10^{-3} | | -2.50×10^{-3} | | $+2.50 \times 10^{-3}$ |
| Final (mol) | 0 | | 0 | | 2.50×10^{-3} |

At the equivalence point, the concentrations of both the acid and the base are zero. The total volume is $(25.0 + 25.0)$ mL, or 50.0 mL, so the concentration of the salt is

$$[\text{NH}_4\text{Cl}] = \frac{2.50 \times 10^{-3} \text{ mol}}{50.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.0500 \text{ mol L}^{-1} = 0.0500 \text{ M}$$

The pH of the solution at the equivalence point is determined by the hydrolysis of NH_4^+ ions:



The expression for K_a is

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = 5.6 \times 10^{-10}$$

If we let $x = [\text{H}^+] = [\text{NH}_3]$, then

$$K_a = \frac{x^2}{0.0500 - x} = 5.6 \times 10^{-10}$$

K_a is small, so we make the approximation $0.0500 - x \approx 0.0500$, giving

$$x = \sqrt{(5.6 \times 10^{-10})(0.0500)} = 5.3 \times 10^{-6} \text{ M}$$

This is much less than 5 percent of 0.0500, so the approximation is valid.

Thus, the pH is

$$\text{pH} = -\log_{10} (5.3 \times 10^{-6}) = 5.28$$

Always check the validity of the approximation.

Check Note that the pH of the solution is acidic. This is what we would expect from the hydrolysis of the ammonium ion.

Practice Exercise Calculate the pH at the equivalence point in the titration of 50 mL of 0.10 M methylamine (see Table 11.4) with a 0.20 M HCl solution.

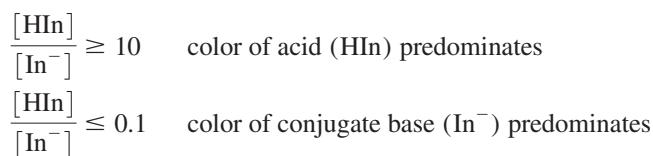
12.4 | An Acid-Base Indicator Is a Substance That Changes Color at a Specific pH

The equivalence point, as we have seen, is the point at which the number of moles of OH^- ions added to a solution is equal to the number of moles of H^+ ions originally present. To determine the equivalence point in a titration, then, we must know exactly how much volume of a base has been added from a buret to an acid in a flask. One way to achieve this goal is to add a few drops of an acid-base indicator to the acid solution at the start of the titration. You will recall from Section 12.3 that an indicator is used to determine the equivalence point of an acid-base titration. An *indicator* is a substance (usually a weak organic acid or base) that has distinctly different colors in its nonionized and ionized forms. Which of these two forms (ionized or nonionized) is dominant depends upon the pH of the solution in which the indicator is dissolved. The *end point* of a titration occurs when the indicator changes color. However, not all indicators change color at the same pH, so the choice of indicator for a particular titration depends on the nature of the acid and base used in the titration (that is, whether they are strong or weak). By choosing the proper indicator for a titration, we can use the end point to determine the equivalence point, as we will see in the following.

Let us consider a weak monoprotic acid that we will call HIn. To be an effective indicator, HIn and its conjugate base, In^- , must have distinctly different colors. In solution, the acid ionizes to a small extent:



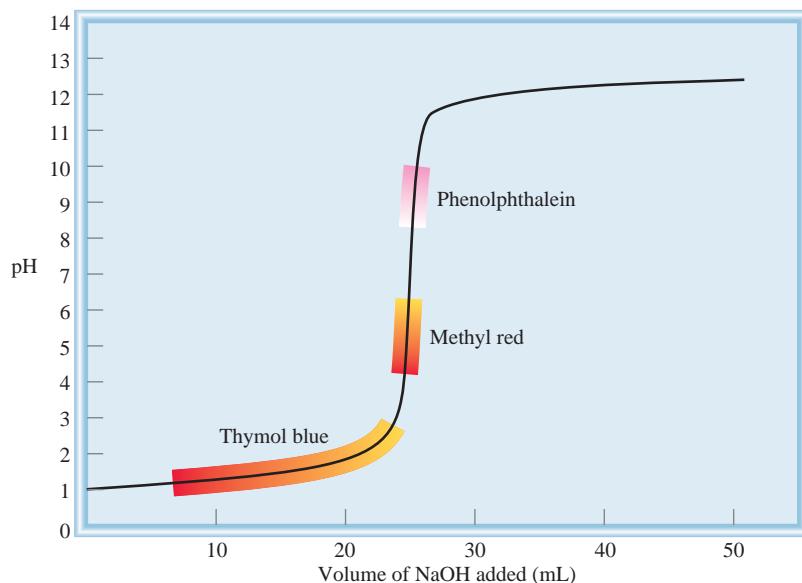
If the indicator is in a sufficiently acidic medium, the equilibrium, according to Le Châtelier's principle, shifts to the left and the predominant color of the indicator is that of the nonionized form (HIn). On the other hand, in a basic medium, the equilibrium shifts to the right, and the color of the solution will be due mainly to that of the conjugate base (In^-). Roughly speaking, we can use the following concentration ratios to predict the perceived color of the indicator:



If $[\text{HIn}] \approx [\text{In}^-]$, then the indicator color is a combination of the colors of HIn and In^- .

The end point of an indicator does not occur at a specific pH; rather, there is a range of pH within which the end point will occur. In practice, we choose an indicator whose end point lies on the steep part of the titration curve, the position of which depends upon the strength of the acid or base being titrated. Because the equivalence point also lies on the steep part of the curve, this choice ensures that the pH at the equivalence point will fall within the range over which the indicator changes color. In Section 12.3, we mentioned that phenolphthalein is a suitable indicator for the titration of NaOH and HCl. Phenolphthalein is colorless in acidic and neutral solutions, but reddish pink in basic solutions. Measurements show that at pH = 8.3 the indicator is colorless but that it begins to turn reddish pink when the pH exceeds 8.3. As shown in Figure 12.5, the steepness of the pH curve near the equivalence point means that the addition of a very small quantity of NaOH (say, 0.05 mL, which is

Figure 12.8 pH curve for the titration of a strong acid with a strong base. Because the indicators methyl red and phenolphthalein have color changes that lie along the steep portion of the curve, they can be used to monitor the equivalence point of the titration. Thymol blue cannot be used for this purpose (see Table 12.1).



about the volume of a drop from the buret) brings about a large rise in the pH of the solution. What is important, however, is the fact that the steep portion of the pH profile includes the range over which phenolphthalein changes from colorless to reddish pink. Whenever such a correspondence occurs, the indicator can be used to locate the equivalence point of the titration (Figure 12.8).

Many acid-base indicators are plant pigments. For example, by boiling chopped red cabbage in water, we can extract pigments that exhibit many different colors at various pHs (Figure 12.9).

Table 12.1 lists a number of indicators commonly used in acid-base titrations. The choice of a particular indicator depends on the strength of the acid and base to be titrated. Example 12.7 illustrates this point.

Figure 12.9 Solutions containing extracts of red cabbage (obtained by boiling the cabbage in water) produce different colors when treated with an acid and a base. The pH of the solutions increases from left to right.



Table 12.1 Some Common Acid-Base Indicators

| Indicator | Color | | pH Range* |
|-------------------|-----------|---------------|-----------|
| | In Acid | In Base | |
| Thymol blue | Red | Yellow | 1.2–2.8 |
| Bromophenol blue | Yellow | Bluish purple | 3.0–4.6 |
| Methyl orange | Orange | Yellow | 3.1–4.4 |
| Methyl red | Red | Yellow | 4.2–6.3 |
| Chlorophenol blue | Yellow | Red | 4.8–6.4 |
| Bromothymol blue | Yellow | Blue | 6.0–7.6 |
| Cresol red | Yellow | Red | 7.2–8.8 |
| Phenolphthalein | Colorless | Reddish pink | 8.3–10.0 |

*The pH range is defined as the range over which the indicator changes from the acid color to the base color.

Example 12.7

Which indicator or indicators listed in Table 12.1 would you use for the acid-base titrations shown in (a) Figure 12.5, (b) Figure 12.6, and (c) Figure 12.7?

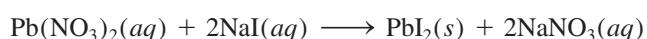
Strategy The choice of an indicator for a particular titration is based on the fact that its pH range for color change must overlap the steep portion of the titration curve. Otherwise, we cannot use the color change to locate the equivalence point.

- Solution** (a) Near the equivalence point, the pH of the solution changes abruptly from 4 to 10. Therefore all the indicators except thymol blue, bromophenol blue, and methyl orange are suitable for use in the titration.
 (b) Here the steep portion covers the pH range between 7 and 10; therefore, the suitable indicators are cresol red and phenolphthalein.
 (c) Here the steep portion of the pH curve covers the pH range between 3 and 7; therefore, the suitable indicators are bromophenol blue, methyl orange, methyl red, and chlorophenol blue.

Practice Exercise Referring to Table 12.1, specify which indicator or indicators you would use for the following titrations: (a) HBr versus CH_3NH_2 , (b) HNO_3 versus NaOH , and (c) HNO_2 versus KOH.

12.5 | A Precipitation Reaction Occurs when a Reaction in Solution Leads to an Insoluble Product

One common type of reaction that occurs in aqueous solution is the **precipitation reaction**, which results in the formation of an insoluble product, or precipitate. A **precipitate** is an insoluble solid that separates from the solution. Precipitation reactions usually involve ionic compounds. For example, when an aqueous solution of lead nitrate $[\text{Pb}(\text{NO}_3)_2]$ is added to an aqueous solution of sodium iodide (NaI), a yellow precipitate of lead iodide (PbI_2) is formed:



BaSO_4 imaging of human large intestine.

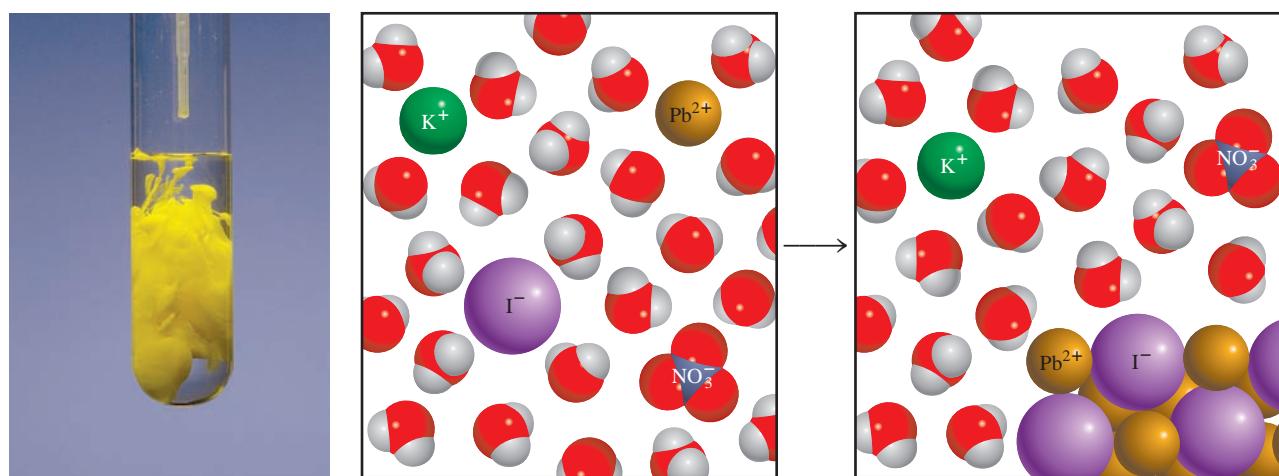


Figure 12.10 The formation of yellow PbI_2 precipitate as a solution of $\text{Pb}(\text{NO}_3)_2$ is added to a solution of NaI .

Sodium nitrate remains in solution. Figure 12.10 shows this reaction in progress.

Precipitation reactions are important in industry, medicine, and everyday life. For example, the preparation of many essential industrial chemicals such as sodium carbonate (Na_2CO_3) is based on precipitation reactions. The dissolving of tooth enamel, which is mainly made of hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3\text{OH}$], in an acidic medium leads to tooth decay. Barium sulfate (BaSO_4), an insoluble compound that is opaque to X rays, is used to diagnose ailments of the digestive tract. Stalactites and stalagmites, which consist of calcium carbonate (CaCO_3), are produced by a precipitation reaction, and so are many foods, such as fudge.

Qualitative Prediction of Solubility

How can we predict whether a precipitate will form when a compound is added to a solution or when two solutions are mixed? It depends on the *solubility* of the solute, which was defined in Section 9.2 as the maximum amount of solute that will dissolve in a given quantity of solvent at a specific temperature and pressure. All ionic compounds are strong electrolytes, but they are not equally soluble. Table 12.2

Table 12.2 Solubility Rules for Common Ionic Compounds in Water at 25°C

| Soluble Compounds | Exceptions |
|---|--|
| Compounds containing alkali metal ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) and the ammonium ion (NH_4^+) Nitrates (NO_3^-), bicarbonates (HCO_3^-), and chlorates (ClO_3^-) Halides (Cl^- , Br^- , I^-) Sulfates (SO_4^{2-}) | Halides of Ag^+ , Hg_2^{2+} , and Pb^{2+} Sulfates of Ag^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Hg_2^{2+} , and Pb^{2+} |
| Insoluble Compounds | Exceptions |
| Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), chromates (CrO_4^{2-}), sulfides (S^{2-}) Hydroxides (OH^-) | Compounds containing alkali metal ions and the ammonium ion Compounds containing alkali metal ions and the Ba^{2+} ion |



Figure 12.11 The appearance of several precipitates. From left to right: CdS, PbS, Ni(OH)₂, and Al(OH)₃.

classifies a number of common ionic compounds as soluble or insoluble. Keep in mind, however, that even insoluble compounds dissolve to a certain extent. Figure 12.11 shows several precipitates.

Example 12.8 applies the solubility rules in Table 12.2.

Example 12.8

Classify the following ionic compounds as soluble or insoluble: (a) silver sulfate (Ag_2SO_4), (b) calcium carbonate (CaCO_3), and (c) sodium phosphate (Na_3PO_4).

Strategy Although it is not necessary to memorize the solubilities of compounds, you should keep in mind the following useful rules: all ionic compounds containing alkali metal cations; the ammonium ion; and the nitrate, bicarbonate, and chlorate ions are soluble. For other compounds, we need to refer to Table 12.2.

- Solution**
- (a) According to Table 12.2, Ag_2SO_4 is insoluble.
 - (b) This is a carbonate and Ca is a Group 2A metal. Therefore, CaCO_3 is insoluble.
 - (c) Sodium is an alkali metal (Group 1A) so Na_3PO_4 is soluble.

Practice Exercise Classify the following ionic compounds as soluble or insoluble:

- (a) CuS, (b) $\text{Ca}(\text{OH})_2$, and (c) $\text{Zn}(\text{NO}_3)_2$.

12.6 | The Solubility Product Is the Equilibrium Constant for the Dissolution Process

Although useful, the solubility rules discussed in Section 12.5 do not allow us to make quantitative predictions about how much of a given ionic compound will dissolve in water. To develop a quantitative approach, we start with what we already know about chemical equilibrium. Unless otherwise stated, in the following discussion the solvent is water and the temperature is 25°C.

The Solubility Product

Consider a saturated solution of silver chloride that is in contact with solid silver chloride. The solubility equilibrium can be represented as



Because salts such as AgCl are considered as strong electrolytes, all the AgCl that dissolves in water is assumed to dissociate completely into Ag^+ and Cl^- ions. Thus, we can write the equilibrium constant for the dissolution of AgCl in terms of the activities of the reactants and products (see Section 10.1):

$$K_{\text{sp}} = \frac{a_{\text{Ag}^+(aq)} a_{\text{Cl}^-(aq)}}{a_{\text{AgCl}(s)}} \quad (12.3)$$

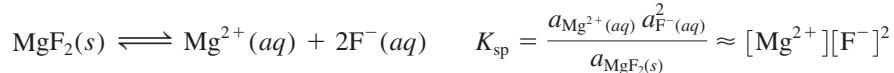
where K_{sp} is called the solubility product constant or simply the *solubility product*. As we saw in Chapter 10, the activity of a pure solid in a reaction can be assumed to a very good approximation to be equal to 1. Also, if the concentrations of solutes are small enough that solute-solute interactions are negligible, then the solution can be considered ideal and we can approximate the activities of those solutes by their concentration relative to the standard concentration (1 mol L^{-1}). With these approximations, Equation 12.3 becomes

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] \quad (12.4)$$

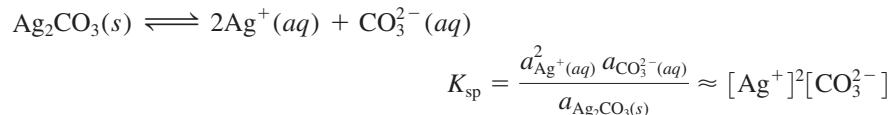
(The concentrations in Equation 12.4 are dimensionless concentrations obtained by dividing the concentrations by 1 mol L^{-1} .) In general, the *solubility product* of a compound can be approximated as *the product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation*. Keep in mind, however, that for solubility equilibria in which the concentration of ions is high ($> 0.001 M$ for singly charged ions, much less for multiply charged ions), the solubilities calculated using Equation 12.4 will differ somewhat from experimentally measured solubilities. It is possible to correct Equation 12.4 by taking into account the deviation of the activity from the molar concentration, but such corrections are beyond the scope of this book.

Because each AgCl unit contains only one Ag^+ ion and one Cl^- ion, its solubility product expression is particularly simple to write. The following cases are slightly more complex:

► MgF_2



► Ag_2CO_3



► $\text{Ca}_3(\text{PO}_4)_2$

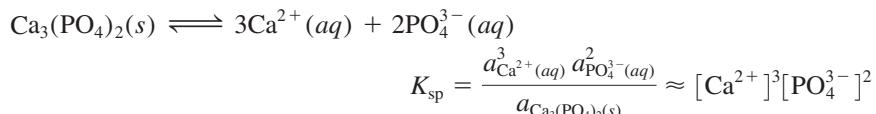


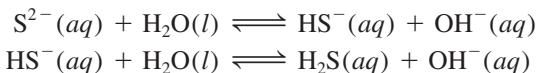
Table 12.3 Solubility Products of Some Slightly Soluble Ionic Compounds at 25°C

| Compound | K_{sp} | Compound | K_{sp} |
|--------------------------------------|-----------------------|----------------------------------|-----------------------|
| Aluminum hydroxide $[Al(OH)_3]$ | 1.8×10^{-33} | Lead(II) chromate $(PbCrO_4)$ | 2.0×10^{-14} |
| Barium carbonate $(BaCO_3)$ | 8.1×10^{-9} | Lead(II) fluoride (PbF_2) | 4.1×10^{-8} |
| Barium fluoride (BaF_2) | 1.7×10^{-6} | Lead(II) iodide (PbI_2) | 1.4×10^{-8} |
| Barium sulfate $(BaSO_4)$ | 1.1×10^{-10} | Lead(II) sulfide (PbS) | 3.4×10^{-28} |
| Bismuth sulfide (Bi_2S_3) | 1.6×10^{-72} | Magnesium carbonate $(MgCO_3)$ | 4.0×10^{-5} |
| Cadmium sulfide (CdS) | 8.0×10^{-28} | Magnesium hydroxide $[Mg(OH)_2]$ | 1.2×10^{-11} |
| Calcium carbonate $(CaCO_3)$ | 8.7×10^{-9} | Manganese(II) sulfide (MnS) | 3.0×10^{-14} |
| Calcium fluoride (CaF_2) | 4.0×10^{-11} | Mercury(I) chloride (Hg_2Cl_2) | 3.5×10^{-18} |
| Calcium hydroxide $[Ca(OH)_2]$ | 8.0×10^{-6} | Mercury(II) sulfide (HgS) | 4.0×10^{-54} |
| Calcium phosphate $[Ca_3(PO_4)_2]$ | 1.2×10^{-26} | Nickel(II) sulfide (NiS) | 1.4×10^{-24} |
| Chromium(III) hydroxide $[Cr(OH)_3]$ | 3.0×10^{-29} | Silver bromide $(AgBr)$ | 7.7×10^{-13} |
| Cobalt(II) sulfide (CoS) | 4.0×10^{-21} | Silver carbonate (Ag_2CO_3) | 8.1×10^{-12} |
| Copper(I) bromide $(CuBr)$ | 4.2×10^{-8} | Silver chloride $(AgCl)$ | 1.6×10^{-10} |
| Copper(I) iodine (CuI) | 5.1×10^{-12} | Silver iodide (AgI) | 8.3×10^{-17} |
| Copper(II) hydroxide $[Cu(OH)_2]$ | 2.2×10^{-20} | Silver sulfate (Ag_2SO_4) | 1.4×10^{-5} |
| Copper(II) sulfide (CuS) | 6.0×10^{-37} | Silver sulfide (Ag_2S) | 6.0×10^{-51} |
| Iron(II) hydroxide $[Fe(OH)_2]$ | 1.6×10^{-14} | Strontium carbonate $(SrCO_3)$ | 1.6×10^{-9} |
| Iron(III) hydroxide $[Fe(OH)_3]$ | 1.1×10^{-36} | Strontium sulfate $(SrSO_4)$ | 3.8×10^{-7} |
| Iron(II) sulfide (FeS) | 6.0×10^{-19} | Tin(II) sulfide (SnS) | 1.0×10^{-26} |
| Lead(II) carbonate $(PbCO_3)$ | 3.3×10^{-14} | Zinc hydroxide $[Zn(OH)_2]$ | 1.8×10^{-14} |
| Lead(II) chloride $(PbCl_2)$ | 2.4×10^{-4} | Zinc sulfide (ZnS) | 3.0×10^{-23} |

Table 12.3 lists the solubility products for a number of salts of low solubility.

Soluble salts such as $NaCl$ and KNO_3 , which have very large K_{sp} values, are not listed in the table for essentially the same reason that K_a values for strong acids are not often reported. The value of K_{sp} indicates the solubility of an ionic compound—the smaller the value, the less soluble the compound in water. However, in using K_{sp} values to compare solubilities, you should choose compounds that have similar formulas, such as $AgCl$ and ZnS , or CaF_2 and $Fe(OH)_2$.

Another factor, in addition to deviations from ideal solution behavior, that can affect the use of K_{sp} in determining solubility is the fact that many anions in the ionic compounds listed in Table 12.3 are conjugate bases of weak acids. Consider copper sulfide (CuS). The S^{2-} ion can hydrolyze as follows



And highly charged small metal ions such as Al^{3+} and Bi^{3+} will undergo hydrolysis as discussed in Section 11.6. In such cases, it is necessary in accurate work to include the hydrolysis equilibrium expressions in addition to the solubility product to determine the equilibrium concentrations of all species in aqueous solution.

For concentrations of ions that do not correspond to equilibrium conditions, we use the reaction quotient (see Section 10.2), which in this case is called the *ion product* (Q), to predict whether a precipitate will form. Note that Q has the same form

as K_{sp} except that the concentrations of ions are *not* equilibrium concentrations. For example, if we mix a solution containing Ag^+ ions with one containing Cl^- ions, then the ion product, assuming ideal solution behavior, is given by

$$Q = [\text{Ag}^+]_0[\text{Cl}^-]_0$$

The subscript 0 reminds us that these are initial concentrations and do not necessarily correspond to those at equilibrium. The possible relationships between Q and K_{sp} are

| | |
|--|---|
| $Q < K_{\text{sp}}$ | unsaturated solution |
| $[\text{Ag}^+]_0[\text{Cl}^-]_0 < 1.6 \times 10^{-10}$ | |
| $Q = K_{\text{sp}}$ | saturated solution (equilibrium) |
| $[\text{Ag}^+]_0[\text{Cl}^-]_0 = 1.6 \times 10^{-10}$ | |
| $Q > K_{\text{sp}}$ | supersaturated solution; AgCl will |
| $[\text{Ag}^+]_0[\text{Cl}^-]_0 > 1.6 \times 10^{-10}$ | precipitate out until the product of the ionic concentrations is equal to 1.6×10^{-10} |

Molar Solubility and Solubility

There are two other ways to express a substance's solubility: **molar solubility**, which is *the number of moles of solute in 1 L of a saturated solution (mol L⁻¹)*, and **solubility**, which is *the number of grams of solute in 1 L of a saturated solution (g L⁻¹)*. Note that both these expressions refer to the concentration of saturated solutions at some given temperature (usually 25°C).

Both molar solubility and solubility are convenient to use in the laboratory. We can use them to determine K_{sp} by following the steps outlined in Figure 12.12(a).

Example 12.9 illustrates this procedure.

Example 12.9

The solubility of calcium sulfate (CaSO_4) is found to be 0.67 g L⁻¹. Calculate the value of K_{sp} for calcium sulfate.

Strategy We are given the solubility of CaSO_4 and asked to calculate its K_{sp} . The sequence of conversion steps, according to Figure 12.12(a), is

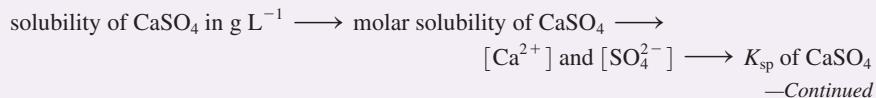
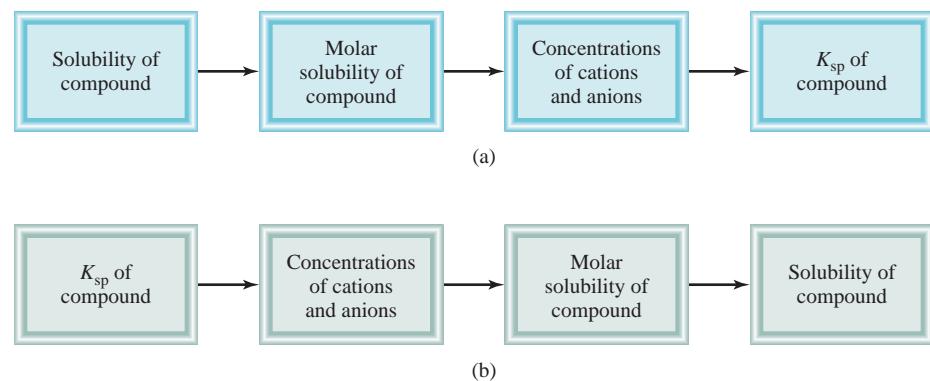


Figure 12.12 The sequence of steps (a) for calculating K_{sp} from solubility data and (b) for calculating solubility from K_{sp} data.



Continued—

Solution Consider the dissociation of CaSO_4 in water. Let s be the molar solubility (in mol L^{-1}) of CaSO_4 .

| $\text{CaSO}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq)$ | | | |
|---|------|------|------|
| Initial (M) | | 0 | 0 |
| Change (M) | $-s$ | $+s$ | $+s$ |
| Equilibrium (M) | | s | s |

The solubility product for CaSO_4 is

$$K_{\text{sp}} \approx [\text{Ca}^{2+}][\text{SO}_4^{2-}] = s^2$$

First, we calculate the number of moles of CaSO_4 dissolved in 1 L of solution

$$\frac{0.67 \text{ g CaSO}_4}{1 \text{ L soln}} \times \frac{1 \text{ mol CaSO}_4}{136.2 \text{ g CaSO}_4} = 4.9 \times 10^{-3} \text{ mol L}^{-1} = s$$

From the solubility equilibrium, we see that for every mole of CaSO_4 that dissolves, 1 mole of Ca^{2+} and 1 mole of SO_4^{2-} are produced. Thus, at equilibrium

$$[\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = s = 4.9 \times 10^{-3} M$$

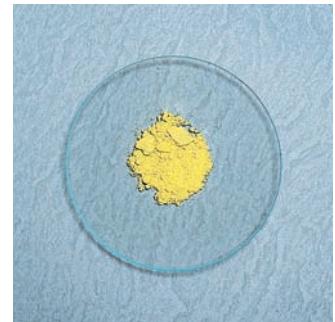
Now we can calculate K_{sp} :

$$\begin{aligned} K_{\text{sp}} &= [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (4.9 \times 10^{-3})(4.9 \times 10^{-3}) \\ &= 2.4 \times 10^{-5} \end{aligned}$$

Practice Exercise The solubility of lead chromate (PbCrO_4) is $4.5 \times 10^{-5} \text{ g L}^{-1}$. Calculate the solubility product of this compound.



Calcium sulfate is used as a drying agent and in the manufacture of paints, ceramics, and paper. A hydrated form of calcium sulfate, called plaster of Paris, is used to make casts for broken bones.



Silver bromide is used in photographic emulsions.

Sometimes we are given the value of K_{sp} for a compound and asked to calculate the compound's molar solubility. For example, the K_{sp} for the dissolution of silver bromide



is 7.7×10^{-13} . We can calculate its molar solubility by the procedure outlined in Figure 12.12(b). First we identify the species present at equilibrium. Here we have Ag^+ and Br^- ions. Let s be the molar solubility (in mol L^{-1}) of AgBr . Because one unit of AgBr yields one Ag^+ and one Br^- ion, at equilibrium, both $[\text{Ag}^+]$ and $[\text{Br}^-]$ are equal to s . Assuming ideal solution behavior, the solubility product expression for this reaction is given by

$$\begin{aligned} K_{\text{sp}} &= [\text{Ag}^+][\text{Br}^-] \\ 7.7 \times 10^{-13} &= s \times s = s^2 \\ s &= \sqrt{7.7 \times 10^{-13}} = 8.8 \times 10^{-7} M \end{aligned}$$

Therefore, at equilibrium

$$[\text{Ag}^+] = [\text{Br}^-] = 8.8 \times 10^{-7} M$$



Copper(II) hydroxide is used as a pesticide and to treat seeds.

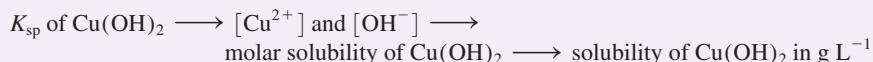
Thus, the molar solubility of AgBr also is $8.8 \times 10^{-7} M$. This concentration is quite small, so the effect of nonideality will be minimal and the use of concentrations in the expression for K_{sp} is accurate.

Example 12.10 makes use of this approach.

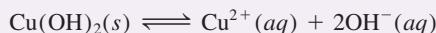
Example 12.10

Using the data in Table 12.3, calculate the solubility of copper(II) hydroxide $[Cu(OH)_2]$ in $g L^{-1}$.

Strategy We are given the K_{sp} of $Cu(OH)_2$ and asked to calculate its solubility in $g L^{-1}$. The sequence of conversion steps, according to Figure 12.12(b), is



Solution Consider the dissociation of $Cu(OH)_2$ in water:



Note that the molar concentration of OH^- is twice that of Cu^{2+} . The solubility product of $Cu(OH)_2$, assuming ideal solution behavior, is

$$\begin{aligned} K_{sp} &= [Cu^{2+}][OH^-]^2 \\ &= (s)(2s)^2 = 4s^3 \end{aligned}$$

From the K_{sp} value in Table 12.3, we solve for the molar solubility of $Cu(OH)_2$ as follows:

$$2.2 \times 10^{-20} = 4s^3$$

and

$$s = \sqrt[3]{\frac{2.2 \times 10^{-20}}{4}} = 1.8 \times 10^{-7} M$$

Finally, from the molar mass of $Cu(OH)_2$ and its molar solubility, we calculate the solubility in $g L^{-1}$:

$$\begin{aligned} \text{solubility of } Cu(OH)_2 &= \frac{1.8 \times 10^{-7} \text{ mol } Cu(OH)_2}{1 \text{ L sol}} \times \frac{97.57 \text{ g } Cu(OH)_2}{1 \text{ mol } Cu(OH)_2} \\ &= 1.8 \times 10^{-5} \text{ g } L^{-1} \end{aligned}$$

Practice Exercise Calculate the solubility of silver chloride ($AgCl$) in $g L^{-1}$.

As Examples 12.9 and 12.10 show, solubility and solubility product are related. If we know one, we can calculate the other, but each quantity provides different information. Table 12.4 shows the relationship between molar solubility and solubility product for a number of ionic compounds, assuming ideal solution behavior.

Predicting Precipitation Reactions

From knowledge of the solubility rules (see Section 12.5) and the solubility products listed in Table 12.3, we can predict whether a precipitate will form when we mix two solutions or add a soluble compound to a solution. This ability often has practical value.

Table 12.4 Relationship Between K_{sp} and Molar Solubility (s)

| Compound | K_{sp} Expression | Cation | Anion | Relation between K_{sp} and s |
|---|--|--------|-------|---|
| AgCl | $[\text{Ag}^+][\text{Cl}^-]$ | s | s | $K_{\text{sp}} = s^2$; $s = (K_{\text{sp}})^{1/2}$ |
| BaSO ₄ | $[\text{Ba}^{2+}][\text{SO}_4^{2-}]$ | s | s | $K_{\text{sp}} = s^2$; $s = (K_{\text{sp}})^{1/2}$ |
| Ag ₂ CO ₃ | $[\text{Ag}^+]^2[\text{CO}_3^{2-}]$ | $2s$ | s | $K_{\text{sp}} = 4s^3$; $s = \left(\frac{K_{\text{sp}}}{4}\right)^{1/3}$ |
| PbF ₂ | $[\text{Pb}^{2+}][\text{F}^-]^2$ | s | $2s$ | $K_{\text{sp}} = 4s^3$; $s = \left(\frac{K_{\text{sp}}}{4}\right)^{1/3}$ |
| Al(OH) ₃ | $[\text{Al}^{3+}][\text{OH}^-]^3$ | s | $3s$ | $K_{\text{sp}} = 27s^4$; $s = \left(\frac{K_{\text{sp}}}{27}\right)^{1/4}$ |
| Ca ₃ (PO ₄) ₂ | $[\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$ | $3s$ | $2s$ | $K_{\text{sp}} = 108s^5$; $s = \left(\frac{K_{\text{sp}}}{108}\right)^{1/5}$ |

In industrial and laboratory preparations, we can adjust the concentrations of ions until the ion product exceeds K_{sp} in order to obtain a given compound (in the form of a precipitate). The ability to predict precipitation reactions is also useful in medicine. For example, kidney stones, which can be extremely painful, consist largely of calcium oxalate (CaC_2O_4 , $K_{\text{sp}} = 2.3 \times 10^{-9}$). The normal physiological concentration of calcium ions in blood plasma is about 5 mM ($1 \text{ mM} = 1 \times 10^{-3} \text{ M}$). Oxalate ions ($\text{C}_2\text{O}_4^{2-}$), derived from oxalic acid present in many vegetables such as rhubarb and spinach, react with the calcium ions to form insoluble calcium oxalate, which can gradually build up in the kidneys. Proper adjustment of a patient's diet can help to reduce precipitate formation. Example 12.11 illustrates the steps involved in predicting precipitation reactions.

Example 12.11

Exactly 200 mL of 0.0040 M BaCl₂ is added to exactly 600 mL of 0.0080 M K₂SO₄. Will a precipitate form?

Strategy Under what condition will an ionic compound precipitate from solution? The ions in solution are Ba²⁺, Cl⁻, K⁺, and SO₄²⁻. According to the solubility rules listed in Table 12.2, the only precipitate that can form is BaSO₄. From the information given, we can calculate [Ba²⁺] and [SO₄²⁻] because we know the number of moles of the ions in the original solutions and the volume of the combined solution.

Next we calculate the reaction quotient $Q = [\text{Ba}^{2+}]_0[\text{SO}_4^{2-}]_0$ and compare the value of Q with the K_{sp} of BaSO₄ to see if a precipitate will form, that is, if the solution is supersaturated.

Solution The number of moles of Ba²⁺ present in the original 200 mL of solution is

$$200 \text{ mL} \times \frac{0.0040 \text{ mol Ba}^{2+}}{1 \text{ L soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 8.0 \times 10^{-4} \text{ mol Ba}^{2+}$$

The total volume after combining the two solutions is 800 mL. The concentration of Ba²⁺ in the 800-mL volume is

$$[\text{Ba}^{2+}] = \frac{8.0 \times 10^{-4} \text{ mol}}{800 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 1.0 \times 10^{-3} \text{ M}$$

—Continued

Continued—

The number of moles of SO_4^{2-} in the original 600 mL of solution is

$$600 \text{ mL} \times \frac{0.0080 \text{ mol } \text{SO}_4^{2-}}{1 \text{ L soln}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 4.8 \times 10^{-3} \text{ mol } \text{SO}_4^{2-}$$

The concentration of SO_4^{2-} in the 800 mL of the combined solution is

$$[\text{SO}_4^{2-}] = \frac{4.8 \times 10^{-3} \text{ mol}}{800 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 6.0 \times 10^{-3} M$$

Now we must compare Q and K_{sp} . From Table 12.3,



As for Q ,

$$Q = [\text{Ba}^{2+}]_0[\text{SO}_4^{2-}]_0 = (1.0 \times 10^{-3})(6.0 \times 10^{-3}) = 6.0 \times 10^{-6}$$

Therefore,

$$Q > K_{\text{sp}}$$

The solution is supersaturated because the value of Q indicates that the concentrations of the ions are too large. Thus, some of the BaSO_4 will precipitate out of solution until

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10}$$

Practice Exercise If 2.00 mL of 0.200 M NaOH is added to 1.00 L of 0.100 M CaCl_2 , will precipitation occur?

Separation of Ions by Fractional Precipitation

In chemical analysis, it is sometimes desirable to remove one type of ion from solution by precipitation while leaving other ions in solution. For instance, the addition of sulfate ions to a solution containing both potassium and barium ions causes BaSO_4 to precipitate out, thereby removing most of the Ba^2 ions from the solution. The other “product,” K_2SO_4 , is soluble and will remain in solution. The BaSO_4 precipitate can be separated from the solution by filtration.

Even when *both* products are insoluble, we can still achieve some degree of separation by choosing the proper reagent to bring about precipitation. Consider a solution that contains Cl^- , Br^- , and I^- ions. One way to separate these ions is to convert them to insoluble silver halides. As the K_{sp} values in Table 12.3 show, the solubility of the halides decreases from AgCl to AgI . Thus, when a soluble compound such as silver nitrate is slowly added to this solution, AgI begins to precipitate first, followed by AgBr and then AgCl .

Example 12.12 describes the separation of only two ions (Cl^- and Br^-), but the procedure can be applied to a solution containing more than two different types of ions if precipitates of differing solubility can be formed.

Example 12.12

Silver nitrate is slowly added to a solution that is 0.020 M in Cl^- ions and 0.020 M in Br^- ions. Calculate the concentration of Ag^+ ions (in mol L^{-1}) required to initiate the precipitation of AgBr without precipitating AgCl .

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Continued—

Strategy In solution, AgNO_3 dissociates into Ag^+ and NO_3^- ions. The Ag^+ ions then combine with the Cl^- and Br^- ions to form AgCl and AgBr precipitates. Because AgBr is less soluble (it has a smaller K_{sp} than that of AgCl), it will precipitate first. Therefore, this is a fractional precipitation problem. Knowing the concentrations of Cl^- and Br^- ions, we can calculate $[\text{Ag}^+]$ from the K_{sp} values. Keep in mind that K_{sp} refers to a saturated solution. To initiate precipitation, $[\text{Ag}^+]$ must exceed the concentration in the saturated solution in each case.

Solution The solubility equilibrium for AgBr is



Because $[\text{Br}^-] = 0.020 \text{ M}$, the concentration of Ag^+ that must be exceeded to initiate the precipitation of AgBr is

$$[\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{Br}^-]} = \frac{7.7 \times 10^{-13}}{0.020} = 3.9 \times 10^{-11} \text{ M}$$

Thus, $[\text{Ag}^+] > 3.9 \times 10^{-11} \text{ M}$ is required to start the precipitation of AgBr .

The solubility equilibrium for AgCl is



so

$$[\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{Cl}^-]} = \frac{1.6 \times 10^{-10}}{0.020} = 8.0 \times 10^{-9} \text{ M}$$

Therefore, $[\text{Ag}^+] > 8.0 \times 10^{-9} \text{ M}$ is required to start the precipitation of AgCl .

To precipitate AgBr without precipitating Cl^- ions then, $[\text{Ag}^+]$ must be greater than $3.9 \times 10^{-11} \text{ M}$ and lower than $8.0 \times 10^{-9} \text{ M}$.

Practice Exercise The solubility products of AgCl and Ag_3PO_4 are 1.6×10^{-10} and 1.8×10^{-18} , respectively. If Ag^+ is added (without changing the volume) to 1.00 L of a solution containing 0.10 mol Cl^- and 0.10 mol PO_4^{3-} , calculate the concentration of Ag^+ ions (in mol L^{-1}) required to initiate (a) the precipitation of AgCl and (b) the precipitation of Ag_3PO_4 .

Example 12.12 raises the question: What is the concentration of Br^- ions remaining in solution just before AgCl begins to precipitate? To answer this question, we let $[\text{Ag}^+] = 8.0 \times 10^{-9} \text{ M}$. Then

$$[\text{Br}^-] = \frac{K_{\text{sp}}}{[\text{Ag}^+]} = \frac{7.7 \times 10^{-13}}{8.0 \times 10^{-9}} = 9.6 \times 10^{-5} \text{ M}$$

The percent of Br^- remaining in solution (the *unprecipitated* Br^-) at the critical concentration of Ag^+ is

$$\begin{aligned} \% \text{ Br}^- &= \frac{[\text{Br}^-]_{\text{unppt'd}}}{[\text{Br}^-]_{\text{original}}} \times 100\% \\ &= \frac{9.6 \times 10^{-5} \text{ M}}{0.020 \text{ M}} \times 100\% \\ &= 0.48\% \text{ unprecipitated} \end{aligned}$$

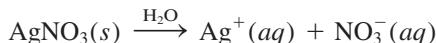
Thus, $(100 - 0.48)$ percent, or 99.52 percent, of Br^- will have precipitated as AgBr just before AgCl begins to precipitate. By this procedure, the Br^- ions can be quantitatively separated from the Cl^- ions.

12.7 | The Solubility of a Substance Is Affected by a Number of Factors

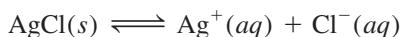
The Common Ion Effect and Solubility

In Section 12.1, we discussed the effect of a common ion on acid and base ionizations. Here we will examine the relationship between the common ion effect and solubility. As we have noted, the solubility product is an equilibrium constant; precipitation of an ionic compound from solution occurs whenever the ion product exceeds K_{sp} for that substance. In a saturated solution of AgCl , for example, the ion product $[\text{Ag}^+][\text{Cl}^-]$ is, of course, equal to K_{sp} . Furthermore, simple stoichiometry tells us that $[\text{Ag}^+] = [\text{Cl}^-]$. But this equality does not hold in all situations.

Suppose we study a solution containing two dissolved substances that share a common ion, say, AgCl and AgNO_3 . In addition to the dissociation of AgCl , the total concentration of the common silver ions in solution is also affected by the dissolution of silver nitrate:



The solubility equilibrium of AgCl is



If AgNO_3 is added to a saturated AgCl solution, the increase in $[\text{Ag}^+]$ will make the ion product greater than the solubility product:

$$Q = [\text{Ag}^+][\text{Cl}^-]_0 > K_{\text{sp}}$$

At a given temperature, only the solubility of a compound is altered (decreased) by the common ion effect. Its solubility product, which is an equilibrium constant, remains the same whether or not other substances are present in the solution.

To reestablish equilibrium, some AgCl will precipitate out of the solution, as Le Châtelier's principle would predict, until the ion product is once again equal to K_{sp} . The effect of adding a common ion, then, is a *decrease* in the solubility of the salt (AgCl) in solution. Note that in this case $[\text{Ag}^+]$ is no longer equal to $[\text{Cl}^-]$ at equilibrium; rather, $[\text{Ag}^+] > [\text{Cl}^-]$.

Example 12.13 shows the common ion effect on solubility.

Example 12.13

Calculate the solubility of silver chloride (in g L^{-1}) in a $6.5 \times 10^{-3} M$ silver nitrate solution.

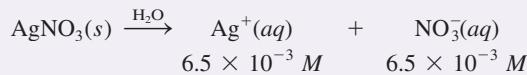
Strategy This is a common-ion problem. The common ion here is Ag^+ , which is supplied by both AgCl and AgNO_3 . Remember that the presence of the common ion will affect only the solubility of AgCl (in g L^{-1}), but not the K_{sp} value because it is an equilibrium constant.

Solution Step 1: The relevant species in solution are Ag^+ ions (from both AgCl and AgNO_3) and Cl^- ions. The NO_3^- ions are spectator ions.

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Continued—

Step 2: Because AgNO_3 is a soluble strong electrolyte, it dissociates completely:



Let s be the molar solubility of AgCl in AgNO_3 solution. We summarize the changes in concentrations as follows:

| $\text{AgCl}(s)$ | \rightleftharpoons | $\text{Ag}^+(aq)$ | + | $\text{Cl}^-(aq)$ |
|---------------------|----------------------|--------------------------|------|-------------------|
| Initial (M) | | 6.5×10^{-3} | | 0.0 |
| Change (M) | | $-s$ | $+s$ | $+s$ |
| Equilibrium (M) | | $6.5 \times 10^{-3} + s$ | | s |

Step 3:

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

$$1.6 \times 10^{-10} = (6.5 \times 10^{-3} + s)s$$

Because AgCl is quite insoluble and the presence of Ag^+ ions from AgNO_3 further lowers the solubility of AgCl , s must be very small compared with 6.5×10^{-3} . Therefore, applying the approximation $6.5 \times 10^{-3} + s \approx 6.5 \times 10^{-3}$, we obtain

$$1.6 \times 10^{-10} = (6.5 \times 10^{-3})s$$

$$s = 2.5 \times 10^{-8} M$$

Step 4: At equilibrium

$$[\text{Ag}^+] = (6.5 \times 10^{-3} + 2.5 \times 10^{-8}) M \approx 6.5 \times 10^{-3} M$$

$$[\text{Cl}^-] = 2.5 \times 10^{-8} M$$

and so our approximation was justified in step 3. Because all the Cl^- ions must come from AgCl , the amount of AgCl dissolved in AgNO_3 solution also is $2.5 \times 10^{-8} M$. Then, knowing the molar mass of AgCl (143.4 g), we can calculate the solubility of AgCl as follows:

$$\text{solubility of AgCl in AgNO}_3 \text{ solution} = \frac{2.5 \times 10^{-8} \text{ mol AgCl}}{1 \text{ L soln}} \times \frac{143.4 \text{ g AgCl}}{1 \text{ mol AgCl}}$$

$$= 3.6 \times 10^{-6} \text{ g L}^{-1}$$

Check The solubility of AgCl in pure water is $1.9 \times 10^{-3} \text{ g L}^{-1}$ (see the Practice Exercise in Example 12.10). Therefore, the lower solubility ($3.6 \times 10^{-6} \text{ g L}^{-1}$) in the presence of AgNO_3 is reasonable. You should also be able to predict the lower solubility using Le Châtelier's principle. Adding Ag^+ ions shifts the equilibrium to the left, thus decreasing the solubility of AgCl .

Practice Exercise Calculate the solubility in g L^{-1} of AgBr in (a) pure water and (b) $0.0010 M \text{ NaBr}$.

pH and Solubility

The solubilities of many substances also depend on the pH of the solution. Consider the solubility equilibrium of magnesium hydroxide:



Adding OH^- ions (increasing the pH) shifts the equilibrium from right to left, thereby decreasing the solubility of $\text{Mg}(\text{OH})_2$. (This is another example of the common ion effect.) On the other hand, adding H^+ ions (decreasing the pH) shifts the equilibrium from left to right, and the solubility of $\text{Mg}(\text{OH})_2$ increases. Thus, insoluble bases tend to dissolve in acidic solutions. Similarly, insoluble acids tend to dissolve in basic solutions.

To explore the quantitative effect of pH on the solubility of $\text{Mg}(\text{OH})_2$, let us first calculate the pH of a saturated $\text{Mg}(\text{OH})_2$ solution. We write

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.2 \times 10^{-11}$$

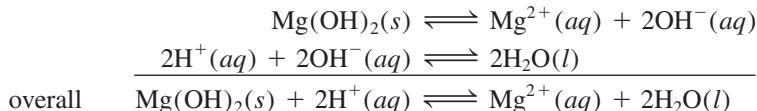
Let s be the molar solubility of $\text{Mg}(\text{OH})_2$. Proceeding as in Example 12.10,

$$\begin{aligned} K_{\text{sp}} &= (s)(2s)^2 = 4s^3 \\ 4s^3 &= 1.2 \times 10^{-11} \\ s &= \sqrt[3]{\frac{1.2 \times 10^{-11}}{4}} = 1.4 \times 10^{-4} \end{aligned}$$

At equilibrium, therefore,

$$\begin{aligned} [\text{OH}^-] &= 2 \times 1.4 \times 10^{-4} M = 2.8 \times 10^{-4} M \\ \text{pOH} &= -\log_{10}(2.8 \times 10^{-4}) = 3.55 \\ \text{pH} &= 14.00 - 3.55 = 10.45 \end{aligned}$$

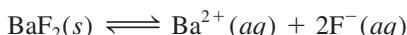
In a medium with a pH of less than 10.45, the solubility of $\text{Mg}(\text{OH})_2$ would increase. This follows from the fact that a lower pH indicates a higher $[\text{H}^+]$ and thus a lower $[\text{OH}^-]$, as we would expect from $K_w = [\text{H}^+][\text{OH}^-]$. Consequently, $[\text{Mg}^{2+}]$ rises to maintain the a saturated solution, and more $\text{Mg}(\text{OH})_2$ dissolves. The dissolution process and the effect of extra H^+ ions can be summarized as follows:



Milk of magnesia, which contains $\text{Mg}(\text{OH})_2$, is used to treat acid indigestion.

If the pH of the medium were higher than 10.45, $[\text{OH}^-]$ would be higher and the solubility of $\text{Mg}(\text{OH})_2$ would decrease because of the common ion (OH^-) effect.

The pH also influences the solubility of salts that contain a basic anion. For example, the solubility equilibrium for BaF_2 is



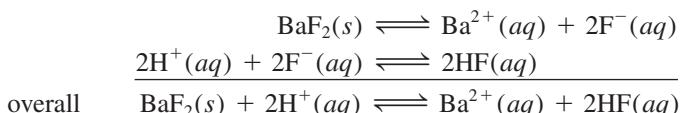
and

$$K_{\text{sp}} = [\text{Ba}^{2+}][\text{F}^-]^2$$

In an acidic medium, the high $[\text{H}^+]$ will shift the following equilibrium from left to right:



As $[\text{F}^-]$ decreases, $[\text{Ba}^{2+}]$ must increase to maintain the equilibrium condition. Thus, more BaF_2 dissolves. The dissolution process and the effect of pH on the solubility of BaF_2 can be summarized as follows:



The solubilities of salts containing anions that do not hydrolyze are unaffected by pH. Examples of such anions are Cl^- , Br^- , and I^- .

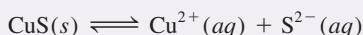
Examples 12.14 and 12.15 deal with the effect of pH on solubility.

Example 12.14

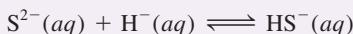
Which of the following compounds will be more soluble in acidic solution than in water: (a) CuS , (b) AgCl , and (c) PbSO_4 ?

Strategy In each case write the dissociation reaction of the salt into its cation and anion. The cation will not interact with the H^+ ion because they both bear positive charges. The anion will act as a proton acceptor only if it is the conjugate base of a weak acid. How would the removal of the anion affect the solubility of the salt?

Solution (a) The solubility equilibrium for CuS is

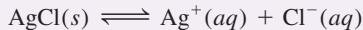


The sulfide ion is a weak base because it is the conjugate base of the weak acid HS^- . Therefore, the S^{2-} ion reacts with the H^+ ion as follows:



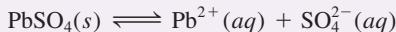
This reaction removes the S^{2-} ions from solution. According to Le Châtelier's principle, the equilibrium will shift to the right to replace some of the S^{2-} ions that were removed, thereby increasing the solubility of CuS .

(b) The solubility equilibrium is

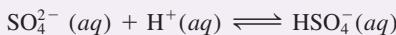


Because Cl^- is the conjugate base of a strong acid (HCl), the solubility of AgCl is not affected by an acid solution.

(c) The solubility equilibrium for PbSO_4 is



The sulfate ion is a weak base because it is the conjugate base of the weak acid HSO_4^{2-} . Therefore, the SO_4^{2-} ion reacts with the H^+ ion as follows:



This reaction removes the SO_4^{2-} ions from solution. According to Le Châtelier's principle, the equilibrium will shift to the right to replace some of the SO_4^{2-} ions that were removed, thereby increasing the solubility of PbSO_4 .

Practice Exercise Are the following compounds more soluble in water or in an acidic solution: (a) $\text{Ca}(\text{OH})_2$, (b) $\text{Mg}_3(\text{PO}_4)_2$, and (c) PbBr_2 ?

Example 12.15

Calculate the concentration of aqueous ammonia necessary to initiate the precipitation of iron(II) hydroxide from a 0.0030 M solution of FeCl_2 .

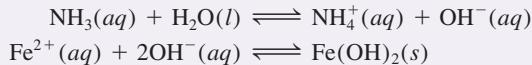
Strategy For iron(II) hydroxide to precipitate from solution, the product $[\text{Fe}^{2+}][\text{OH}^-]^2$ must be greater than its K_{sp} . First, we calculate $[\text{OH}^-]$ from the known

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Continued—

$[Fe^{2+}]$ and the K_{sp} value listed in Table 12.3. This is the concentration of OH^- in a saturated solution of $Fe(OH)_2$. Next, we calculate the concentration of NH_3 that will supply this concentration of OH^- ions. Finally, any NH_3 concentration greater than the calculated value will initiate the precipitation of $Fe(OH)_2$ because the solution will become supersaturated.

Solution Ammonia reacts with water to produce OH^- ions, which then react with Fe^{2+} to form $Fe(OH)_2$. The equilibria of interest are



First, we find the OH^- concentration above which $Fe(OH)_2$ begins to precipitate. We write

$$K_{sp} = [Fe^{2+}][OH^-]^2 = 1.6 \times 10^{-14}$$

Because $FeCl_2$ is a strong electrolyte, $[Fe^{2+}] = 0.0030\ M$ and

$$\begin{aligned} [OH^-]^2 &= \frac{1.6 \times 10^{-14}}{0.0030} = 5.3 \times 10^{-12} \\ [OH^-] &= 2.3 \times 10^{-6}\ M \end{aligned}$$

Next, we calculate the concentration of the weak base NH_3 that will supply $2.3 \times 10^{-6}\ M\ OH^-$ ions.

Let x be the initial concentration of NH_3 in $mol\ L^{-1}$. We summarize the changes in concentrations resulting from the ionization of NH_3 as follows:

| | $NH_3(aq) + H_2O(l)$ | \rightleftharpoons | $NH_4^+(aq)$ | + | $OH^-(aq)$ |
|---------------------|--------------------------|----------------------|-----------------------|-----------------------|------------|
| Initial (M) | x | | 0.00 | | 0.00 |
| Change (M) | -2.3×10^{-6} | | $+2.3 \times 10^{-6}$ | $+2.3 \times 10^{-6}$ | |
| Equilibrium (M) | $x - 2.3 \times 10^{-6}$ | | 2.3×10^{-6} | 2.3×10^{-6} | |

The equilibrium concentrations of NH_3 , OH^- , and NH_4^+ are then related by the base ionization constant for NH_3 (which from Table 11.4 is equal to 1.8×10^{-5}):

$$\begin{aligned} K_b &= \frac{[NH_4^+][OH^-]}{[NH_3]} \\ 1.8 \times 10^{-5} &= \frac{(2.3 \times 10^{-6})(2.3 \times 10^{-6})}{x - 2.3 \times 10^{-6}} \end{aligned}$$

Solving for x , we obtain

$$x = 2.6 \times 10^{-6}\ M$$

Therefore, the concentration of NH_3 must be slightly greater than $2.6 \times 10^{-6}\ M$ to initiate the precipitation of $Fe(OH)_2$.

Practice Exercise Calculate whether or not a precipitate will form if 2.0 mL of 0.60 $M\ NH_3$ is added to 1.0 L of $1.0 \times 10^{-3}\ M\ FeSO_4$.

Complex Ion Equilibria and Solubility

Lewis acids and bases are discussed in Section 11.1.

Lewis acid-base reactions in which a metal cation combines with a Lewis base result in the formation of complex ions. Thus, we can define a **complex ion** as an ion containing a central metal cation bonded to one or more molecules or ions. Complex

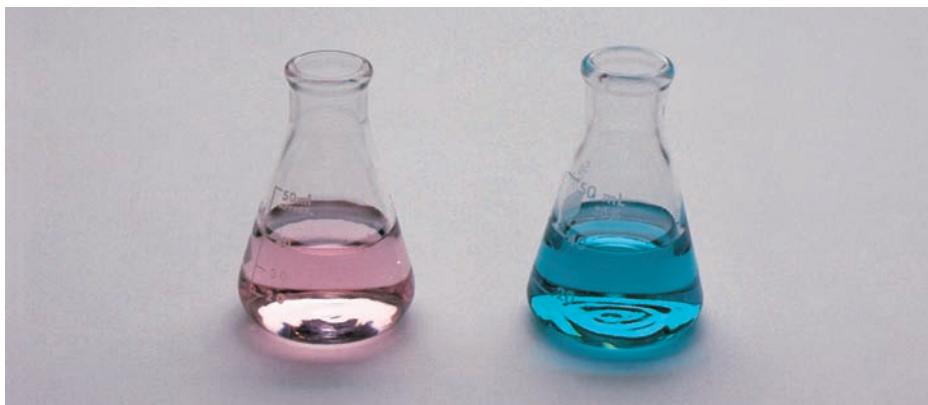
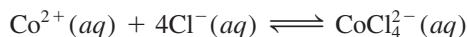


Figure 12.13 Left: An aqueous cobalt(II) chloride solution. The pink color is due to the presence of $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ions. Right: After the addition of HCl solution, the solution turns blue because of the formation of the complex ion CoCl_4^{2-} .

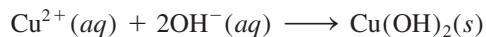
ions are crucial to many chemical and biological processes. Here we will consider the effect of complex ion formation on solubility. In Chapter 15, we will discuss the chemistry of complex ions in more detail.

Transition metals have a particular tendency to form complex ions because they have more than one possible valence state. This property allows them to act effectively as Lewis acids in reactions with many molecules or ions that serve as electron donors (Lewis bases). For example, a solution of cobalt(II) chloride is pink because of the presence of the $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ions (Figure 12.13).

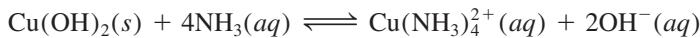
When HCl is added, the solution turns blue as a result of the formation of the complex ion CoCl_4^{2-} :



Copper(II) sulfate (CuSO_4) dissolves in water to produce a blue solution. The hydrated copper(II) ions are responsible for this color; many other sulfates (Na_2SO_4 , for example) are colorless. Adding a few drops of concentrated ammonia solution to a CuSO_4 solution causes the formation of a light-blue precipitate, copper(II) hydroxide:



The OH^- ions are supplied by the ammonia solution. If more NH_3 is added, the blue precipitate redissolves to produce a beautiful dark-blue solution, this time due to the formation of the complex ion $\text{Cu}(\text{NH}_3)_4^{2+}$ (Figure 12.14):



According to our definition, $\text{Co}(\text{H}_2\text{O})_6^{2+}$ is itself a complex ion. When we write $\text{Co}(\text{H}_2\text{O})_6^{2+}$, we mean the hydrated Co^{2+} ion.



Figure 12.14 Left: An aqueous solution of copper(II) sulfate. Center: After the addition of a few drops of a concentrated aqueous ammonia solution, a light-blue precipitate of $\text{Cu}(\text{OH})_2$ is formed. Right: When more concentrated aqueous ammonia solution is added, the $\text{Cu}(\text{OH})_2$ precipitate dissolves to form the dark-blue complex ion $\text{Cu}(\text{NH}_3)_4^{2+}$.

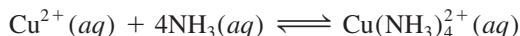
Table 12.5 Formation Constants of Select Complex Ions in Water at 25°C

| Complex Ion | Equilibrium Expression | Formation Constant (K_f) |
|---------------------------------|--|------------------------------|
| $\text{Ag}(\text{NH}_3)_2^+$ | $\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+$ | 1.5×10^7 |
| $\text{Ag}(\text{CN})_2^-$ | $\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons \text{Ag}(\text{CN})_2^-$ | 1.0×10^{21} |
| $\text{Cu}(\text{CN})_4^{2-}$ | $\text{Cu}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Cu}(\text{CN})_4^{2-}$ | 1.0×10^{25} |
| $\text{Cu}(\text{NH}_3)_4^{2+}$ | $\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$ | 5.0×10^{13} |
| $\text{Cd}(\text{CN})_4^{2-}$ | $\text{Cd}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Cd}(\text{CN})_4^{2-}$ | 7.1×10^{16} |
| CdI_4^{2-} | $\text{Cd}^{2+} + 4\text{I}^- \rightleftharpoons \text{CdI}_4^{2-}$ | 2.0×10^6 |
| HgCl_4^{2-} | $\text{Hg}^{2+} + 4\text{Cl}^- \rightleftharpoons \text{HgCl}_4^{2-}$ | 1.7×10^{16} |
| HgI_4^{2-} | $\text{Hg}^{2+} + 4\text{I}^- \rightleftharpoons \text{HgI}_4^{2-}$ | 2.0×10^{30} |
| $\text{Hg}(\text{CN})_4^{2-}$ | $\text{Hg}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Hg}(\text{CN})_4^{2-}$ | 2.5×10^{41} |
| $\text{Co}(\text{NH}_3)_6^{3+}$ | $\text{Co}^{3+} + 6\text{NH}_3 \rightleftharpoons \text{Co}(\text{NH}_3)_6^{3+}$ | 5.0×10^{31} |
| $\text{Zn}(\text{NH}_3)_4^{2+}$ | $\text{Zn}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Zn}(\text{NH}_3)_4^{2+}$ | 2.9×10^9 |

Thus, the formation of the complex ion $\text{Cu}(\text{NH}_3)_4^{2+}$ increases the solubility of $\text{Cu}(\text{OH})_2$.

A measure of the tendency of a metal ion to form a particular complex ion is given by the **formation constant** K_f (also called the *stability constant*), which is the *equilibrium constant for the complex ion formation*. The larger the value of K_f , the more stable the complex ion. Table 12.5 lists the formation constants of a number of complex ions.

The formation of the $\text{Cu}(\text{NH}_3)_4^{2+}$ ion can be expressed as



for which the formation constant, assuming ideal solution behavior, is

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = 5.0 \times 10^{13}$$

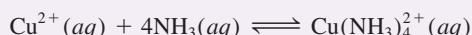
The very large value of K_f in this case indicates that the complex ion is quite stable in solution and accounts for the very low concentration of copper(II) ions at equilibrium.

The use of formation constants to determine aqueous equilibrium in solutions that exhibit complex ion formation is illustrated in Example 12.16.

Example 12.16

A 0.20-mole quantity of CuSO_4 is added to a liter of 1.20 M NH_3 solution. What is the concentration of Cu^{2+} ions at equilibrium?

Strategy The addition of CuSO_4 to the NH_3 solution results in complex ion formation:



—Continued

Continued—

From Table 12.5, we see that the formation constant (K_f) for this reaction is very large; therefore, the reaction lies mostly to the right. At equilibrium, the concentration of Cu^{2+} will be very small. As a good approximation, we can assume that essentially all the dissolved Cu^{2+} ions end up as $\text{Cu}(\text{NH}_3)_4^{2+}$ ions. How many moles of NH_3 will react with 0.20 mole of Cu^{2+} ? How many moles of $\text{Cu}(\text{NH}_3)_4^{2+}$ will be produced? A very small amount of Cu^{2+} will be present at equilibrium. Set up the K_f expression for the preceding equilibrium to solve for $[\text{Cu}^{2+}]$.

Solution The amount of NH_3 consumed in forming the complex ion is $4 \times 0.20 \text{ mol}$, or 0.80 mol. (Note that 0.20 mol Cu^{2+} is initially present in solution and four NH_3 molecules are needed to form a complex ion with one Cu^{2+} ion.) The concentration of NH_3 at equilibrium is therefore $(1.20 - 0.80) \text{ mol L}^{-1}$ soln or 0.40 M , and that of $\text{Cu}(\text{NH}_3)_4^{2+}$ is 0.20 mol L^{-1} soln or 0.20 M , the same as the initial concentration of Cu^{2+} . [There is a 1:1 mole ratio between the initial value of Cu^{2+} and the final value of $\text{Cu}(\text{NH}_3)_4^{2+}$.] Because $\text{Cu}(\text{NH}_3)_4^{2+}$ does dissociate to a slight extent, we call the concentration of Cu^{2+} at equilibrium x and write

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$

$$5.0 \times 10^{13} = \frac{0.20}{x(0.40)^4}$$

Solving for x and keeping in mind that the volume of the solution is 1 L, we obtain

$$x = 1.6 \times 10^{-13} \text{ M} = [\text{Cu}^{2+}]$$

Check The small value of $[\text{Cu}^{2+}]$ at equilibrium, compared with 0.20 M , certainly justifies our approximation.

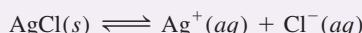
Practice Exercise If 2.50 g of CuSO_4 is dissolved in $9.0 \times 10^2 \text{ mL}$ of 0.30 M NH_3 , what are the concentrations of Cu^{2+} , $\text{Cu}(\text{NH}_3)_4^{2+}$, and NH_3 at equilibrium?

The effect of complex ion formation generally is to *increase* the solubility of a substance, as Example 12.17 shows.

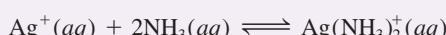
Example 12.17

Calculate the molar solubility of AgCl in a 1.0 M NH_3 solution.

Strategy AgCl is only slightly soluble in water:



The Ag^+ ions form a complex ion with NH_3 (see Table 12.5):



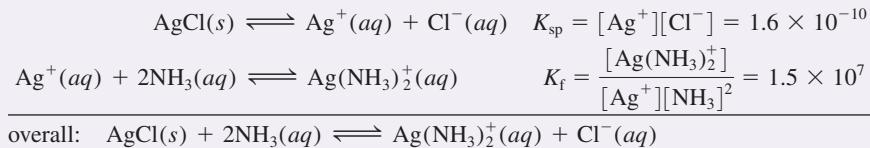
Combining these two equilibria will give the overall equilibrium for the process.

Solution *Step 1:* Initially, the species in solution are Ag^+ and Cl^- ions and NH_3 . The reaction between Ag^+ and NH_3 produces the complex ion $\text{Ag}(\text{NH}_3)_2^+$.

—Continued

Continued—

Step 2: The equilibrium reactions are



The equilibrium constant K for the overall reaction is the product of the equilibrium constants of the individual reactions (see Section 10.2):

$$\begin{aligned} K &= K_{\text{sp}}K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} \\ &= (1.6 \times 10^{-10})(1.5 \times 10^7) \\ &= 2.4 \times 10^{-3} \end{aligned}$$

Let s be the molar solubility of AgCl (mol L⁻¹). We summarize the changes in concentrations that result from the formation of the complex ion as follows:

| | | $\text{AgCl}(s) + 2\text{NH}_3(aq)$ | \rightleftharpoons | $\text{Ag}(\text{NH}_3)_2^+(aq)$ | $+ \text{Cl}^-(aq)$ | |
|--|--|-------------------------------------|----------------------|----------------------------------|---------------------|------|
| | | Initial (M) | | 0.0 | 0.0 | |
| | | Change (M) | | $-s$ | $-2s$ | $+s$ |
| | | Equilibrium (M) | | $1.0 - 2s$ | s | s |

The formation constant for $\text{Ag}(\text{NH}_3)_2^+$ is quite large, so most of the silver ions exist in the complexed form. In the absence of ammonia we have, at equilibrium, $[\text{Ag}^+] = [\text{Cl}^-]$. As a result of complex ion formation, however, we can write $[\text{Ag}(\text{NH}_3)_2^+] = [\text{Cl}^-]$.

$$\begin{aligned} \text{Step 3:} \quad K &= \frac{(s)(s)}{(1.0 - 2s)^2} \\ 2.4 \times 10^{-3} &= \frac{s^2}{(1.0 - 2s)^2} \end{aligned}$$

Taking the square root of both sides, we obtain

$$\begin{aligned} 0.049 &= \frac{s}{1.0 - 2s} \\ s &= 0.045 \text{ M} \end{aligned}$$

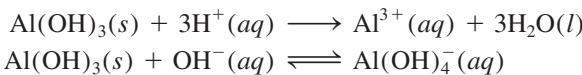
Therefore, at equilibrium, 0.045 mole of AgCl dissolves in 1 L of 1.0 M NH₃ solution.

Check The molar solubility of AgCl in pure water is 1.3×10^{-5} M. Thus, the formation of the complex ion $\text{Ag}(\text{NH}_3)_2^+$ enhances the solubility of AgCl (Figure 12.15).

Practice Exercise Calculate the molar solubility of AgBr in a 1.0 M NH₃ solution.

All amphoteric hydroxides are insoluble compounds.

Finally, we note that there is a class of hydroxides, called *amphoteric hydroxides*, that can react with both acids and bases. Examples are Al(OH)₃, Pb(OH)₂, Cr(OH)₃, Zn(OH)₂, and Cd(OH)₂. Thus, Al(OH)₃ reacts with acids and bases as follows:



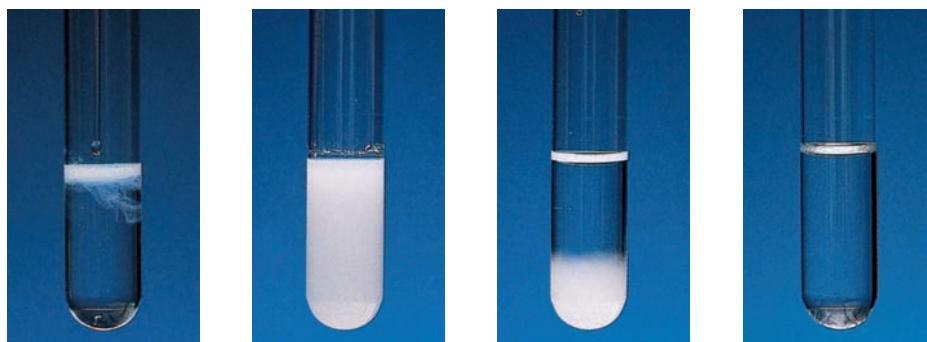


Figure 12.15 From left to right: The formation of AgCl precipitate when AgNO₃ solution is added to NaCl solution. With the addition of NH₃ solution, the AgCl precipitate dissolves as the soluble Ag(NH₃)₂⁺ forms.

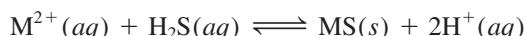
The increase in solubility of Al(OH)₃ in a basic medium is the result of the formation of the complex ion Al(OH)₄⁻ in which Al(OH)₃ acts as the Lewis acid and OH⁻ acts as the Lewis base. Other amphoteric hydroxides behave in a similar manner.

12.8 | The Solubility Product Principle Can Be Applied to Qualitative Analysis

Here we will briefly discuss *qualitative analysis*, *the determination of the types of ions present in a solution*. We will focus on the cations. There are some 20 common cations that can be analyzed readily in aqueous solution. These cations can be divided into five groups according to the solubility products of their insoluble salts (Table 12.6). Because an unknown solution may contain from 1 to all 20 ions, any analysis must be carried out systematically from group 1 through group 5. Let us consider the general procedure for separating these 20 ions by adding precipitating reagents to an unknown solution.

Do not confuse the groups in Table 12.6, which are based on solubility products, with those in the periodic table, which are based on the electron configurations of the elements.

- ▶ **Group 1 Cations.** When dilute HCl is added to the unknown solution, only the Ag, Hg₂²⁺, and Pb²⁺ ions precipitate as insoluble chlorides. The other ions, whose chlorides are soluble, remain in solution.
- ▶ **Group 2 Cations.** After the chloride precipitates have been removed by filtration, hydrogen sulfide is reacted with the unknown acidic solution. Under this condition, the concentration of the S²⁻ ion in solution is negligible. Therefore, the precipitation of metal sulfides is best represented as



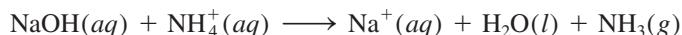
Adding acid to the solution shifts this equilibrium to the left so that only the least soluble metal sulfides, that is, those with the smallest K_{sp} values, will precipitate out of solution. These are Bi₂S₃, CdS, CuS, HgS, and SnS (see Table 12.6).

- ▶ **Group 3 Cations.** At this stage, sodium hydroxide is added to the solution to make it basic. In a basic solution, the equilibrium between M²⁺ and MS shifts to the right. Therefore, the more soluble sulfides (CoS, FeS, MnS, NiS, and ZnS) now precipitate out of solution. Note that the Al³⁺ and Cr³⁺ ions actually precipitate as the hydroxides Al(OH)₃ and Cr(OH)₃, rather than as the sulfides, because the hydroxides are less soluble. The solution is then filtered to remove the insoluble sulfides and hydroxides.
- ▶ **Group 4 Cations.** After all the group 1, 2, and 3 cations have been removed from solution, sodium carbonate is added to the basic solution to precipitate Ba²⁺, Ca²⁺, and Sr²⁺ ions as BaCO₃, CaCO₃, and SrCO₃. These precipitates too are removed from solution by filtration.

Table 12.6 Separation of Cations into Groups According to Their Precipitation Reactions with Various Reagents

| Group | Cation | Precipitating Reagents | Insoluble Compound | K_{sp} |
|-------|--------------------|--|--------------------------|-----------------------|
| 1 | Ag^+ | HCl | AgCl | 1.6×10^{-10} |
| | Hg_2^{2+} | | Hg_2Cl_2 | 3.5×10^{-18} |
| | Pb^{2+} | | PbCl_2 | 2.4×10^{-4} |
| 2 | Bi^{3+} | H_2S in acidic solutions | Bi_2S_3 | 1.6×10^{-72} |
| | Cd^{2+} | | CdS | 8.0×10^{-28} |
| | Cu^{2+} | | CuS | 6.0×10^{-37} |
| | Hg^{2+} | | HgS | 4.0×10^{-54} |
| | Sn^{2+} | | SnS | 1.0×10^{-26} |
| 3 | Al^{3+} | H_2S in basic solutions | $\text{Al}(\text{OH})_3$ | 1.8×10^{-33} |
| | Co^{2+} | | CoS | 4.0×10^{-21} |
| | Cr^{3+} | | $\text{Cr}(\text{OH})_3$ | 3.0×10^{-29} |
| | Fe^{2+} | | FeS | 6.0×10^{-19} |
| | Mn^{2+} | | MnS | 3.0×10^{-14} |
| | Ni^{2+} | | NiS | 1.4×10^{-24} |
| | Zn^{2+} | | ZnS | 3.0×10^{-23} |
| 4 | Ba^{2+} | Na_2CO_3 | BaCO_3 | 8.1×10^{-9} |
| | Ca^{2+} | | CaCO_3 | 8.7×10^{-9} |
| | Sr^{2+} | | SrCO_3 | 1.6×10^{-9} |
| 5 | K^+ | No precipitating reagent | None | |
| | Na^+ | | None | |
| | NH_4^+ | | None | |

► **Group 5 Cations.** At this stage, the only cations possibly remaining in solution are Na^+ , K^+ , and NH_4^+ . The presence of NH_4^+ can be determined by adding sodium hydroxide:



The ammonia gas is detected either by noting its characteristic odor or by observing a piece of wet red litmus paper turning blue when placed above (not in contact with) the solution. To confirm the presence of Na^+ and K^+ ions, we usually use a flame test, as follows: A piece of platinum wire (chosen because platinum is inert) is moistened with the solution and is then held over a Bunsen burner flame. Each type of metal ion gives a characteristic color when heated in this manner. For example, the color emitted by Na^+ ions is yellow, that of K^+ ions is violet, and that of Cu^{2+} ions is green (Figure 12.16).

Figure 12.17 summarizes this scheme for separating metal ions.

Two points regarding qualitative analysis must be mentioned. First, the separation of the cations into groups is made as selective as possible, that is, the anions that are added as reagents must be such that they will precipitate the fewest types of cations. For example, all the cations in group 1 also form insoluble sulfides. Thus, if H_2S were

Because NaOH is added in group 3 and Na_2CO_3 is added in group 4, the flame test for Na^+ ions must be carried out on the original solution.



Figure 12.16 Left to right: Flame colors of lithium, sodium, potassium, and copper.

reacted with the solution at the start, as many as seven different sulfides might precipitate out of solution (group 1 *and* group 2 sulfides), an undesirable outcome. Second, the removal of cations at each step must be carried out as completely as possible. For example, if we do not add enough HCl to the unknown solution to remove all the group 1 cations, they will precipitate with the group 2 cations as insoluble sulfides, interfering with further chemical analysis and leading to erroneous conclusions.

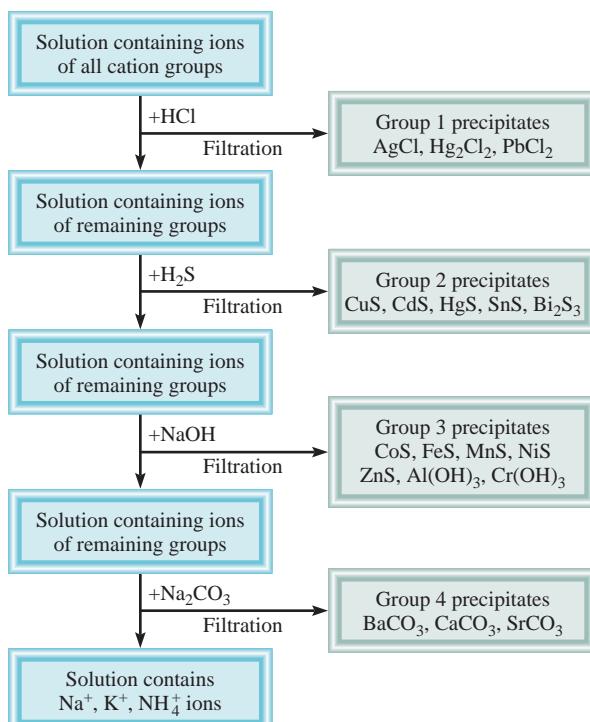


Figure 12.17 A flowchart for the separation of cations in qualitative analysis.

Summary of Facts and Concepts

Section 12.1

- The common ion effect tends to suppress the ionization of a weak acid or a weak base. This action can be explained by Le Châtelier's principle.

Section 12.2

- A buffer solution is a combination of either a weak acid and its weak conjugate base (supplied by a salt) or a weak base and its weak conjugate acid (supplied by a salt); the solution reacts with small amounts of added acid or base in such a way that the pH of the solution remains nearly constant. Buffer systems play a vital role in maintaining the pH of body fluids.

Section 12.3

- The pH at the equivalence point of an acid-base titration depends on hydrolysis of the salt formed in the neutralization reaction. For strong acid-strong base titrations, the pH at the equivalence point is 7; for weak acid-strong base titrations, the pH at the equivalence point is greater than 7; for strong acid-weak base titrations, the pH at the equivalence point is less than 7.

Section 12.4

- Acid-base indicators are weak organic acids or bases that change color near the equivalence point in an acid-base neutralization reaction.
- The specific indicator suitable for a particular titration will depend upon the pH of the end point.

Key Words

buffer solution, p. 615
common ion effect, p. 612
complex ion, p. 648
end point, p. 631
equivalence point, p. 623

formation constant, p. 650
Henderson-Hasselbalch equation, p. 613
indicator, p. 631
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precipitate, p. 633
precipitation reaction, p. 633
qualitative analysis, p. 653
solubility, p. 638
solubility product, p. 636

standard solution, p. 622
titration, p. 622

Problems²

The Ionization of Weak Acids and Bases Is Suppressed by the Addition of a Common Ion

- 12.1 Determine the pH of (a) a 0.40 M CH_3COOH solution, and (b) a solution that is 0.40 M CH_3COOH and 0.20 M CH_3COONa .
- 12.2 Determine the pH of (a) a 0.20 M NH_3 solution, and (b) a solution that is 0.20 M in NH_3 and 0.30 M NH_4Cl .

Section 12.5

- From general rules about the solubilities of ionic compounds, we can predict qualitatively whether a precipitate will form in a reaction.

Section 12.6

- The solubility product K_{sp} is the equilibrium constant for the dissolution of a solid into a solution. Solubility can be estimated from K_{sp} and vice versa.

Section 12.7

- The presence of a common ion decreases the solubility of a slightly soluble salt.
- The solubility of slightly soluble salts containing basic anions increases as the hydrogen ion activity (or concentration) increases. The solubility of salts with anions derived from strong acids is unaffected by pH.
- Complex ions are formed in solution by the combination of a metal cation with a Lewis base. The formation constant K_f measures the tendency toward the formation of a specific complex ion. Complex ion formation can increase the solubility of an insoluble substance.

Section 12.8

- Qualitative analysis is used to identify cations and anions in solution.

The pH of a Buffer Solution Is Resistant to Large Changes in pH

- 12.3 Which of the following solutions can act as a buffer:
(a) KCl/HCl , (b) $\text{KHSO}_4/\text{H}_2\text{SO}_4$, (c) $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$, (d) $\text{KNO}_2/\text{HNO}_2$, and (e) $\text{KHSO}_3/\text{K}_2\text{SO}_4$?
- 12.4 Which of the following solutions can act as a buffer:
(a) KCN/HCN , (b) $\text{Na}_2\text{SO}_4/\text{NaHSO}_4$, (c) $\text{NH}_3/\text{NH}_4\text{NO}_3$, and (d) NaI/HI ?

2. Unless otherwise stated, assume that the temperature in these problems is 25°C.

- 12.5 Calculate the pH of the buffer system made up of 0.15 M $\text{NH}_3/0.35\text{ M}$ NH_4Cl .
- 12.6 Calculate the pH of the following two buffer solutions: (a) 2.0 M $\text{CH}_3\text{COONa}/2.0\text{ M}$ CH_3COOH , and (b) 0.20 M $\text{CH}_3\text{COONa}/0.20\text{ M}$ CH_3COOH . State any approximations made in this calculation. Which is the more effective buffer? Why?
- 12.7 The pH of a bicarbonate–carbonic acid buffer is 8.00. Calculate the ratio of the concentration of carbonic acid (H_2CO_3) to that of the bicarbonate ion (HCO_3^-).
- 12.8 What is the pH of the buffer 0.10 M $\text{Na}_2\text{HPO}_4/0.15\text{ M}$ KH_2PO_4 ?
- 12.9 The pH of a sodium acetate–acetic acid buffer is 4.50. Calculate the ratio $[\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}]$.
- 12.10 The pH of blood plasma is 7.40. Assuming the principal buffer system is $\text{HCO}_3^-/\text{H}_2\text{CO}_3$, calculate the ratio $[\text{HCO}_3^-]/[\text{H}_2\text{CO}_3]$. Is this buffer more effective against an added acid or an added base?
- 12.11 Calculate the pH of the 0.20 M $\text{NH}_3/0.20\text{ M}$ NH_4Cl buffer. What is the pH of the buffer after the addition of 10.0 mL of 0.10 M HCl to 65.0 mL of the buffer?
- 12.12 Calculate the pH of 1.00 L of the buffer 1.00 M $\text{CH}_3\text{COONa}/1.00\text{ M}$ CH_3COOH before and after the addition of (a) 0.080 mol NaOH, and (b) 0.12 mol HCl. (Assume that there is no change in volume.)
- 12.13 A diprotic acid, H_2A , has the following ionization constants: $K_{\text{a}_1} = 1.1 \times 10^{-3}$ and $K_{\text{a}_2} = 2.5 \times 10^{-6}$. In order to make up a buffer solution of pH 5.80, which combination would you choose: $\text{NaHA}/\text{H}_2\text{A}$ or $\text{Na}_2\text{A}/\text{NaHA}$?
- 12.14 A student is asked to prepare a buffer solution at pH = 8.60, using one of the following weak acids: HA ($K_{\text{a}} = 2.7 \times 10^{-3}$), HB ($K_{\text{a}} = 4.4 \times 10^{-6}$), HC ($K_{\text{a}} = 2.6 \times 10^{-9}$). Which acid should she choose? Why?
- 12.19 A 0.1276-g sample of an unknown monoprotic acid was dissolved in 25.0 mL of water and titrated with 0.0633 M NaOH solution. The volume of base required to bring the solution to the equivalence point was 18.4 mL . (a) Calculate the molar mass of the acid. (b) After 10.0 mL of base had been added during the titration, the pH was determined to be 5.87. What is the K_{a} of the unknown acid?
- 12.20 A solution is made by mixing exactly 500 mL of 0.167 M NaOH with exactly 500 mL of 0.100 M CH_3COOH . Calculate the equilibrium concentrations of H^+ , CH_3COOH , CH_3COO^- , OH^- , and Na^+ .
- 12.21 Calculate the pH at the equivalence point for the following titration: 0.20 M HCl versus 0.20 M methylamine (CH_3NH_2).
- 12.22 Calculate the pH at the equivalence point for the following titration: 0.10 M HCOOH versus 0.10 M NaOH.
- 12.23 A 25.0-mL solution of 0.100 M CH_3COOH is titrated with a 0.200 M KOH solution. Calculate the pH after the following additions of the KOH solution: (a) 0.0 mL , (b) 5.0 mL , (c) 10.0 mL , (d) 12.5 mL , and (e) 15.0 mL .
- 12.24 A 10.0-mL solution of 0.300 M NH_3 is titrated with a 0.100 M HCl solution. Calculate the pH after the following additions of the HCl solution: (a) 0.0 mL , (b) 10.0 mL , (c) 20.0 mL , (d) 30.0 mL , and (e) 40.0 mL .

An Acid-Base Indicator Is a Substance That Changes Color at a Specific pH

- The Concentration of an Unknown Acid or Base Can Be Determined by Titration**
- 12.15 A 0.2688-g sample of a monoprotic acid neutralizes 16.4 mL of 0.08133 M KOH solution. Calculate the molar mass of the acid.
- 12.16 A 5.00-g quantity of a diprotic acid was dissolved in water and made up to exactly 250 mL . Calculate the molar mass of the acid if 25.0 mL of this solution required 11.1 mL of 1.00 M KOH for neutralization. Assume that both protons of the acid were titrated.
- 12.17 In a titration experiment, 12.5 mL of 0.500 M H_2SO_4 neutralizes 50.0 mL of NaOH. What is the concentration of the NaOH solution?
- 12.18 In a titration experiment, 20.4 mL of 0.883 M HCOOH neutralizes 19.3 mL of $\text{Ba}(\text{OH})_2$. What is the concentration of the $\text{Ba}(\text{OH})_2$ solution?

- 12.25 Referring to Table 12.1, specify which indicator or indicators you would use for the following titrations: (a) HCOOH versus NaOH, (b) HCl versus KOH, and (c) HNO_3 versus CH_3NH_2 .
- 12.26 A student carried out an acid-base titration by adding NaOH solution from a buret to an Erlenmeyer flask containing HCl solution and using phenolphthalein as indicator. At the equivalence point, she observed a faint reddish-pink color. However, after a few minutes, the solution gradually turned colorless. What do you suppose happened?
- 12.27 The ionization constant K_{a} of an indicator HIn is 1.0×10^{-6} . The color of the nonionized form is red and that of the ionized form is yellow. What is the color of this indicator in a solution whose pH is 4.00?
- 12.28 The K_{a} of a certain indicator is 2.0×10^{-6} . The color of HIn is green and that of In^- is red. A few drops of the indicator are added to an HCl solution, which is then titrated against an NaOH solution. At what pH will the indicator change color?

A Precipitation Reaction Occurs when a Reaction in Solution Leads to an Insoluble Product

- 12.29 Characterize the following compounds as soluble or insoluble in water: (a) $\text{Ca}_3(\text{PO}_4)_2$, (b) $\text{Mn}(\text{OH})_2$, (c) AgClO_3 , and (d) K_2S .
- 12.30 Characterize the following compounds as soluble or insoluble in water: (a) CaCO_3 , (b) ZnSO_4 , (c) $\text{Hg}(\text{NO}_3)_2$, (d) HgSO_4 , and (e) NH_4ClO_4 .
- 12.31 Which of the following processes will likely result in a precipitation reaction? (a) Mixing an NaNO_3 solution with a CuSO_4 solution. (b) Mixing a BaCl_2 solution with a K_2SO_4 solution. Write a net ionic equation for the precipitation reaction.
- 12.32 An ionic compound X is only slightly soluble in water. What test would you employ to show that the compound does indeed dissolve in water to a certain extent?
- 12.33 A 0.9157-g mixture of CaBr_2 and NaBr is dissolved in water, and AgNO_3 is added to the solution to form AgBr precipitate. If the mass of the precipitate is 1.6930 g, what is the percent by mass of NaBr in the original mixture?

The Solubility Product Is the Equilibrium Constant for the Dissolution Process

- 12.34 Calculate the concentration of ions in the following saturated solutions: (a) $[\text{I}^-]$ in AgI solution with $[\text{Ag}^+] = 9.1 \times 10^{-9} \text{ M}$, and (b) $[\text{Al}^{3+}]$ in $\text{Al}(\text{OH})_3$ solution with $[\text{OH}^-] = 2.9 \times 10^{-9} \text{ M}$.
- 12.35 From the solubility data given, calculate the solubility products for the following compounds: (a) SrF_2 , $7.3 \times 10^{-2} \text{ g L}^{-1}$, and (b) Ag_3PO_4 , $6.7 \times 10^{-3} \text{ g L}^{-1}$.
- 12.36 The molar solubility of MnCO_3 is $4.2 \times 10^{-6} \text{ M}$. What is the K_{sp} for this compound? The solubility of an ionic compound MX (molar mass = 346 g) is $4.63 \times 10^{-3} \text{ g L}^{-1}$. What is the K_{sp} for the compound?
- 12.37 The solubility of an ionic compound M_2X_3 (molar mass = 288 g) is $3.6 \times 10^{-17} \text{ g L}^{-1}$. What is the K_{sp} for the compound?
- 12.38 Using data from Table 12.3, calculate the molar solubility of CaF_2 .
- 12.39 What is the pH of a saturated zinc hydroxide solution?
- 12.40 The pH of a saturated solution of a metal hydroxide MOH is 9.68. Calculate the K_{sp} for the compound.
- 12.41 If 20.0 mL of 0.10 M $\text{Ba}(\text{NO}_3)_2$ is added to 50.0 mL of 0.10 M Na_2CO_3 , will BaCO_3 precipitate?
- 12.42 A volume of 75 mL of 0.060 M NaF is mixed with 25 mL of 0.15 M $\text{Sr}(\text{NO}_3)_2$. Calculate the concentrations in the final solution of NO_3^- , Na^+ , Sr^{2+} , and F^- . (K_{sp} for SrF_2 is 2.0×10^{-10} .)

- 12.43 Solid NaI is slowly added to a solution that is 0.010 M in Cu^+ and 0.010 M in Ag^+ . (a) Which compound will begin to precipitate first? (b) Calculate $[\text{Ag}^+]$ when CuI just begins to precipitate. (c) What percent of Ag^+ remains in solution at this point?
- 12.44 Find the approximate pH range suitable for the separation of Fe^{3+} and Zn^{2+} ions by precipitation of $\text{Fe}(\text{OH})_3$ from a solution that is initially 0.010 M in both Fe^{3+} and Zn^{2+} .

The Solubility of a Substance Is Affected by a Number of Factors

- 12.45 How does the common ion effect influence solubility equilibria? Use Le Châtelier's principle to explain the decrease in solubility of CaCO_3 in an Na_2CO_3 solution.
- 12.46 The molar solubility of AgCl in $6.5 \times 10^{-3} \text{ M}$ AgNO_3 is $2.5 \times 10^{-8} \text{ M}$. In deriving K_{sp} from these data, which of the following assumptions are reasonable? (a) K_{sp} is the same as solubility. (b) K_{sp} of AgCl is the same in $6.5 \times 10^{-3} \text{ M}$ AgNO_3 as in pure water. (c) Solubility of AgCl is independent of the concentration of AgNO_3 . (d) $[\text{Ag}^+]$ in solution does not change significantly upon the addition of AgCl to $6.5 \times 10^{-3} \text{ M}$ AgNO_3 . (e) $[\text{Ag}^+]$ in solution after the addition of AgCl to $6.5 \times 10^{-3} \text{ M}$ AgNO_3 is the same as it would be in pure water.
- 12.47 How many grams of CaCO_3 will dissolve in $3.0 \times 10^{-2} \text{ mL}$ of 0.050 M $\text{Ca}(\text{NO}_3)_2$?
- 12.48 The solubility product of PbBr_2 is 8.9×10^{-6} . Determine the molar solubility (a) in pure water, (b) in 0.20 M KBr solution, and (c) in 0.20 M $\text{Pb}(\text{NO}_3)_2$ solution.
- 12.49 Calculate the molar solubility of AgCl in a 1.00-L solution containing 10.0 g of dissolved CaCl_2 .
- 12.50 Calculate the molar solubility of BaSO_4 (a) in water, and (b) in a solution containing 1.0 M SO_4^{2-} ions.
- 12.51 Which of the following ionic compounds will be more soluble in acid solution than in water: (a) BaSO_4 , (b) PbCl_2 , (c) $\text{Fe}(\text{OH})_3$, or (d) CaCO_3 ?
- 12.52 Which of the following will be more soluble in acid solution than in pure water: (a) CuI , (b) Ag_2SO_4 , (c) $\text{Zn}(\text{OH})_2$, (d) BaC_2O_4 , or (e) $\text{Ca}_3(\text{PO}_4)_2$?
- 12.53 Compare the molar solubility of $\text{Mg}(\text{OH})_2$ in water and in a solution buffered at a pH of 9.0.
- 12.54 Calculate the molar solubility of $\text{Fe}(\text{OH})_2$ in a solution buffered at (a) pH 8.00, and (b) pH 10.00.
- 12.55 The solubility product of $\text{Mg}(\text{OH})_2$ is 1.2×10^{-11} . What minimum OH^- concentration must be attained

- (e.g., by adding NaOH) to decrease the Mg^{2+} concentration in a solution of $Mg(NO_3)_2$ to less than $1.0 \times 10^{-10} M$?
- 12.56 Calculate whether or not a precipitate will form if 2.00 mL of 0.60 M NH_3 are added to 1.0 L of $1.0 \times 10^{-3} M$ $FeSO_4$.
- 12.57 If 2.50 g of $CuSO_4$ are dissolved in 9.0×10^{-2} mL of 0.30 M NH_3 , what are the concentrations of Cu^{2+} , $Cu(NH_3)_4^{2-}$, and NH_3 at equilibrium? Calculate the concentrations of Cd^{2+} , $Cd(CN)_4^{2-}$, and CN^- at equilibrium when 0.50 g of $Cd(NO_3)_2$ dissolves in 5.0×10^{-2} mL of 0.50 M NaCN.
- 12.58 If NaOH is added to 0.010 M Al^{3+} , which will be the predominant species at equilibrium: $Al(OH)_3$ or $Al(OH)_4^-$? The pH of the solution is 14.00. [K_f for $Al(OH)_4^-$ is 2.0×10^{-33} .]
- 12.59 Calculate the molar solubility of AgI in a 1.0 M NH_3 solution.
- 12.60 Both Ag^+ and Zn^{2+} form complex ions with NH_3 . Write balanced equations for the reactions. However, $Zn(OH)_2$ is soluble in 6 M NaOH, and $AgOH$ is not. Explain.
- 12.61 Explain, with balanced ionic equations, why (a) CuI_2 dissolves in ammonia solution, (b) $AgBr$ dissolves in NaCN solution, and (c) $HgCl_2$ dissolves in KCl solution.
- 12.68 Sketch the titration curve of a weak acid versus a strong base like the one shown in Figure 12.6. On your graph indicate the volume of base used at the equivalence point and also at the half-equivalence point, that is, the point at which half of the acid has been neutralized. Show how you can measure the pH of the solution at the half-equivalence point. Using Equation 12.2, explain how you can determine the pK_a of the acid by this procedure.
- 12.69 A 200-mL volume of NaOH solution was added to 400 mL of a 2.00 M HNO_2 solution. The pH of the mixed solution was 1.50 units greater than that of the NaOH solution. Calculate the molarity of the NaOH solution.
- 12.70 The pK_a of butyric acid (HBut) is 4.7. Calculate K_b for the butyrate ion (But^-).
- 12.71 A solution is made by mixing exactly 500 mL of 0.167 M NaOH with exactly 500 mL 0.100 M $HCOOH$. Calculate the equilibrium concentrations of H^+ , $HCOOH$, $HCOO^-$, OH^- , and Na^+ .
- 12.72 $Cd(OH)_2$ is an insoluble compound. It dissolves in excess NaOH in solution. Write a balanced ionic equation for this reaction. What type of reaction is this?
- 12.73 A student mixes 50.0 mL of 1.00 M $Ba(OH)_2$ with 86.4 mL of 0.494 M H_2SO_4 . Calculate the mass of $BaSO_4$ formed and the pH of the mixed solution.
- 12.74 For which of the following reactions is the equilibrium constant called a solubility product?
- $Zn(OH)_2(s) + 2OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$
 - $3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \rightleftharpoons Ca_3(PO_4)_2(s)$
 - $CaCO_3(s) + 2H^+(aq) \rightleftharpoons Ca^{2+}(aq) + H_2O(l) + CO_2(g)$
 - $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$
- 12.75 A 2.0-L kettle contains 116 g of boiler scale ($CaCO_3$). How many times would the kettle have to be completely filled with distilled water to remove all the deposit at 25°C?
- 12.76 Equal volumes of 0.12 M $AgNO_3$ and 0.14 M $ZnCl_2$ solution are mixed. Calculate the equilibrium concentrations of Ag^+ , Cl^- , Zn^{2+} , and NO_3^- .
- 12.77 Calculate the solubility (in $g\ L^{-1}$) of Ag_2CO_3 .
- 12.78 Find the approximate pH range suitable for separating Mg^{2+} and Zn^{2+} by the precipitation of $Zn(OH)_2$ from a solution that is initially 0.010 M in Mg^{2+} and Zn^{2+} .
- 12.79 A volume of 25.0 mL of 0.100 M HCl is titrated against a 0.100 M CH_3NH_2 solution added to it from a buret. Calculate the pH values of the solution (a) after 10.0 mL of CH_3NH_2 solution have been added, (b) after 25.0 mL of CH_3NH_2 solution have been added, and (c) after 35.0 mL of CH_3NH_2 solution have been added.

The Solubility Product Principle Can Be Applied to Qualitative Analysis

- 12.62 In a group 1 analysis, a student obtained a precipitate containing both $AgCl$ and $PbCl_2$. Suggest one reagent that would allow her to separate $AgCl(s)$ from $PbCl_2(s)$.
- 12.63 In a group 1 analysis, a student adds HCl acid to the unknown solution to make $[Cl^-] = 0.15\ M$. Some $PbCl_2$ precipitates. Calculate the concentration of Pb^{2+} remaining in solution.
- 12.64 Both KCl and NH_4Cl are white solids. Suggest one reagent that would enable you to distinguish between these two compounds.
- 12.65 Describe a simple test that would allow you to distinguish between $AgNO_3(s)$ and $Cu(NO_3)_2(s)$.

Additional Problems

- 12.66 The buffer range is defined by the equation

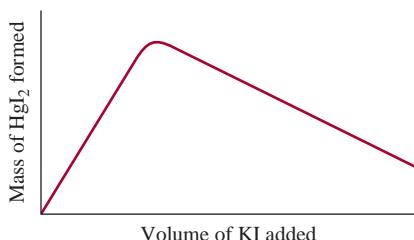
$$pH - pK_a = 1$$

Calculate the range of the ratio [conjugate base]/[acid] that corresponds to this equation.

- 12.67 The pK_a of the indicator methyl orange is 3.46. Over what pH range does this indicator change from 90 percent HIn to 90 percent In^- ?

- 12.80 The molar solubility of $\text{Pb}(\text{IO}_3)_2$ in a 0.10 M NaIO_3 solution is $2.4 \times 10^{-11}\text{ mol L}^{-1}$. What is the K_{sp} for $\text{Pb}(\text{IO}_3)_2$?

- 12.81 When a KI solution was added to a solution of mercury(II) chloride, a precipitate [mercury(II) iodide] formed. A student plotted the mass of the precipitate versus the volume of the KI solution added and obtained the following graph. Explain the appearance of the graph.



- 12.82 Barium is a toxic substance that can seriously impair heart function. For an X-ray of the gastrointestinal tract, a patient drinks an aqueous suspension of 20 g BaSO_4 . If this substance were to equilibrate with the 5.0 L of the blood in the patient's body, what would be $[\text{Ba}^{2+}]$? For a good estimate, we may assume that the temperature is at 25°C . Why is $\text{Ba}(\text{NO}_3)_2$ not chosen for this procedure?

- 12.83 The pK_a of phenolphthalein is 9.10. Over what pH range does this indicator change from 95 percent HIn to 95 percent In^- ?

- 12.84 Solid NaBr is slowly added to a solution that is 0.010 M in Cu^{2+} and 0.010 M in Ag^+ . (a) Which compound will begin to precipitate first? (b) Calculate $[\text{Ag}^+]$ when CuBr just begins to precipitate. (c) What percent of Ag^+ remains in solution at this point?

- 12.85 Cacodylic acid is $(\text{CH}_3)_2\text{AsO}_2\text{H}$. Its ionization constant is 6.4×10^{-7} . (a) Calculate the pH of 50.0 mL of a 0.10 M solution of the acid. (b) Calculate the pH of 25.0 mL of 0.15 M $(\text{CH}_3)_2\text{AsO}_2\text{Na}$. (c) Mix the solutions in parts (a) and (b). Calculate the pH of the resulting solution.

- 12.86 Radiochemical techniques are useful in estimating the solubility product of many compounds. In one experiment, 50.0 mL of a 0.010 M AgNO_3 solution containing a silver isotope with a radioactivity of 74,025 counts per min per mL were mixed with 100 mL of a 0.030 M NaIO_3 solution. The mixed solution was diluted to 500 mL and filtered to remove all the AgIO_3 precipitate. The remaining solution was found to have a radioactivity of 44.4 counts per min per mL. What is the K_{sp} of AgIO_3 ?

- 12.87 The molar mass of a certain metal carbonate, MCO_3 , can be determined by adding an excess of HCl acid to react with all the carbonate and then “back-

titrating” the remaining acid with NaOH. (a) Write an equation for these reactions. (b) In a certain MCO_3 experiment, 20.00 mL of 0.0800 M HCl were added to a 0.1022-g sample of MCO_3 . The excess HCl required 5.64 mL of 0.1000 M NaOH for neutralization. Calculate the molar mass of the carbonate, and identify M.

- 12.88 Acid-base reactions usually go to completion. Confirm this statement by calculating the equilibrium constant for each of the following cases: (a) A strong acid reacting with a strong base. (b) A strong acid reacting with a weak base (NH_3). (c) A weak acid (CH_3COOH) reacting with a strong base. (d) A weak acid (CH_3COOH) reacting with a weak base (NH_3). (Hint: Strong acids exist as H^+ ions and strong bases exist as OH^- ions in solution. You need to look up K_a , K_b , and K_w .)

- 12.89 Calculate x , the number of molecules of water in oxalic acid hydrate ($\text{H}_2\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$) from the following data: 5.00 g of the compound is made up to exactly 250 mL of solution, and 25.0 mL of this solution requires 15.9 mL of 0.500 M NaOH solution for neutralization.

- 12.90 Describe how you would prepare a 1-L 0.20 M $\text{CH}_3\text{COONa}/0.20\text{ M}$ CH_3COOH buffer system by (a) mixing a solution of CH_3COOH with a solution of CH_3COONa , (b) reacting a solution of CH_3COOH with a solution of NaOH, and (c) reacting a solution of CH_3COONa with a solution of HCl.

- 12.91 Phenolphthalein is the common indicator for the titration of a strong acid with a strong base. (a) If the pK_a of phenolphthalein is 9.10, what is the ratio of the nonionized form of the indicator (colorless) to the ionized form (reddish pink) at pH 8.00? (b) If 2 drops of 0.060 M phenolphthalein are used in a titration involving a 50.0-mL volume, what is the concentration of the ionized form at pH 8.00? (Assume that 1 drop = 0.050 mL.)

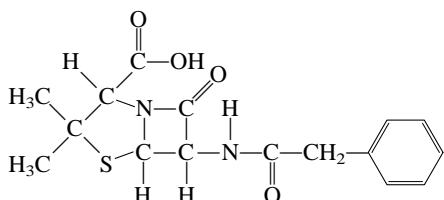
- 12.92 Oil paintings containing lead(II) compounds as constituents of their pigments darken over the years. Suggest a chemical reason for the color change.

- 12.93 What reagents would you employ to separate the following pairs of ions in solution: (a) Na^+ and Ba^{2+} , (b) K^+ and Pb^{2+} , and (c) Zn^{2+} and Hg^{2+} ?

- 12.94 Look up the K_{sp} values for BaSO_4 and SrSO_4 in Table 12.3. Calculate the concentrations of Ba^{2+} , Sr^{2+} , and SO_4^{2-} in a solution that is saturated with both compounds.

- 12.95 In principle, amphoteric oxides, such as Al_2O_3 and BeO , can be used to prepare buffer solutions because they possess both acidic and basic properties (see Section 12.7). Explain why these compounds are of little practical use as buffer components.

- 12.96 CaSO_4 ($K_{\text{sp}} = 2.4 \times 10^{-5}$) has a larger K_{sp} value than that of Ag_2SO_4 ($K_{\text{sp}} = 1.4 \times 10^{-5}$). Does it follow that CaSO_4 also has greater solubility (g L⁻¹)?
- 12.97 When lemon juice is squirted into tea, the color becomes lighter. In part, the color change is due to dilution, but the main reason for the change is an acid-base reaction. What is the reaction? (Hint: Tea contains “polyphenols” that are weak acids and lemon juice contains citric acid.)
- 12.98 How many milliliters of 1.0 M NaOH must be added to a 200 mL solution of 0.10 M NaH_2PO_4 to make a buffer solution with a pH of 7.50?
- 12.99 The maximum allowable concentration of Pb^{2+} ions in drinking water is 0.05 ppm (i.e., 0.05 g of Pb^{2+} in one million grams of water). Is this guideline exceeded if an underground water supply is at equilibrium with the mineral anglesite (PbSO_4 , $K_{\text{sp}} = 1.6 \times 10^{-8}$)?
- 12.100 One of the most common antibiotics is penicillin G (benzylpenicillanic acid), which has the following structure:



It is a weak monoprotic acid:



where HP denotes the parent acid and P⁻ the conjugate base. Penicillin G is produced by growing molds in fermentation tanks at 25°C and a pH range of 4.5 to 5.0. The crude form of this antibiotic is obtained by extracting the fermentation broth with an organic solvent in which the acid is soluble. (a) Identify the acidic hydrogen atom. (b) In one stage of purification, the organic extract of the crude penicillin G is treated with a buffer solution at pH = 6.50. What is the ratio of the conjugate base of penicillin G to the acid at this pH? Would you expect the conjugate base to be more soluble in water than the acid? (c) Penicillin G is not suitable for oral administration, but the sodium salt (NaP) is because it is soluble. Calculate the pH of a 0.12 M NaP solution formed when a tablet containing the salt is dissolved in a glass of water.

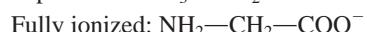
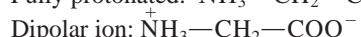
- 12.101 Which of the following solutions has the highest [H⁺]: (a) 0.10 M HF, (b) 0.10 M HF in 0.10 M NaF, or (c) 0.10 M HF in 0.10 M SbF₅? (Hint: SbF₅ reacts with F⁻ to form the complex ion SbF₆⁻.)

- 12.102 Distribution curves show how the fractions of nonionized acid and its conjugate base vary as a function of pH of the medium. Plot distribution curves for CH₃COOH and its conjugate base CH₃COO⁻ in solution. Your graph should show fraction as the y axis and pH as the x axis. What are the fractions and pH at the point where these two curves intersect?
- 12.103 Water containing Ca²⁺ and Mg²⁺ ions is called *hard water* and is unsuitable for some household and industrial use because these ions react with soap to form insoluble salts, or curds. One way to remove the Ca²⁺ ions from hard water is by adding washing soda ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$). (a) The molar solubility of CaCO₃ is 9.3×10^{-5} M. What is its molar solubility in a 0.050 M Na₂CO₃ solution? (b) Why are Mg²⁺ ions not removed by this procedure? (c) The Mg²⁺ ions are removed as Mg(OH)₂ by adding slaked lime [Ca(OH)₂] to the water to produce a saturated solution. Calculate the pH of a saturated Ca(OH)₂ solution. (d) What is the concentration of Mg²⁺ ions at this pH? (e) In general, which ion (Ca²⁺ or Mg²⁺) would you remove first? Why?
- 12.104 Consider the ionization of the following acid-base indicator:



The indicator changes color according to the ratios of the concentrations of the acid to its conjugate base as described on p. 631. Show that the pH range over which the indicator changes from the acid color to the base color is pH = $pK_a \pm 1$, where K_a is the ionization constant of the acid.

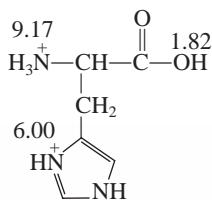
- 12.105 Amino acids are the building blocks of proteins. These compounds contain at least one amino group (—NH₂) and one carboxyl group (—COOH). Consider glycine (NH₂CH₂COOH). Depending on the pH of the solution, glycine can exist in one of three possible forms:



Predict the predominant form of glycine at pH 1.0, 7.0, and 12.0. The pK_a of the carboxyl group is 2.3 and that of the ammonium group (—NH₃⁺) is 9.6.

- 12.106 (a) Referring to Figure 12.7, describe how you would determine the pK_b of the base. (b) Derive an analogous Henderson-Hasselbalch equation relating pOH to pK_b of a weak base B and its conjugate acid HB⁺. Sketch a titration curve showing the variation of the pOH of the base solution versus the volume of a strong acid added from a buret. Describe how you would determine the pK_b from this curve.

- 12.107 One way to distinguish a buffer solution from an acid solution is by dilution. (a) Consider a buffer solution made of 0.500 M CH₃COOH and 0.500 M CH₃COONa. Calculate its pH and the pH after it has been diluted 10-fold. (b) Compare the result in part (a) with the pHs of a 0.500 M CH₃COOH solution before and after it has been diluted in the same manner.
- 12.108 Draw distribution curves for an aqueous carbonic acid solution. Your graph should show fraction of species present as the y axis and pH as the x axis. Note that at any pH, only two of the three species (H₂CO₃, HCO₃⁻, and CO₃²⁻) are present in appreciable concentrations. Use the pK_a values in Table 11.3.
- 12.109 A sample of 0.96 L HCl at 372 mmHg and 22°C is bubbled into 0.034 L of 0.57 M NH₃. What is the pH of the resulting solution? Assume the volume of solution remains constant and that the HCl is totally dissolved in the solution.
- 12.110 Histidine is one of the 20 amino acids found in proteins. Shown here is a fully protonated histidine molecule where the numbers denote the pK_a values of the acidic groups.



- (a) Show stepwise the ionization of histidine in solution.
- (b) A dipolar ion is one in which the species has an equal number of positive and negative charges. Identify the dipolar ion in part (a).
- (c) The pH at which the dipolar ion predominates is called the isoelectric point, denoted by *pI*. The isoelectric point is the average of the pK_a values leading to and following the formation of the dipolar ion. Calculate the *pI* of histidine.
- (d) The histidine group plays an important role in buffering blood. Which conjugate acid-base pair shown in part (a) is responsible for this action?

- 12.111 A 1.0-L saturated silver carbonate solution at 5°C is treated with enough hydrochloric acid to decompose the compound. The carbon dioxide generated is collected in a 19-mL vial and exerts a pressure of 114 mmHg at 25°C. What is the *K*_{sp} of Ag₂CO₃ at 5°C?
- 12.112 Using the value of *K*_{sp} for AgCl given in Table 12.3, estimate the value of *K*_{sp} for this compound at 50°C. What approximations did you make in this calculation? Does the solubility go up or down with increasing temperature? Does this trend follow from Le Châtelier's principle? (The enthalpy of solution for AgCl is 65.7 kJ mol⁻¹ at 25°C.)

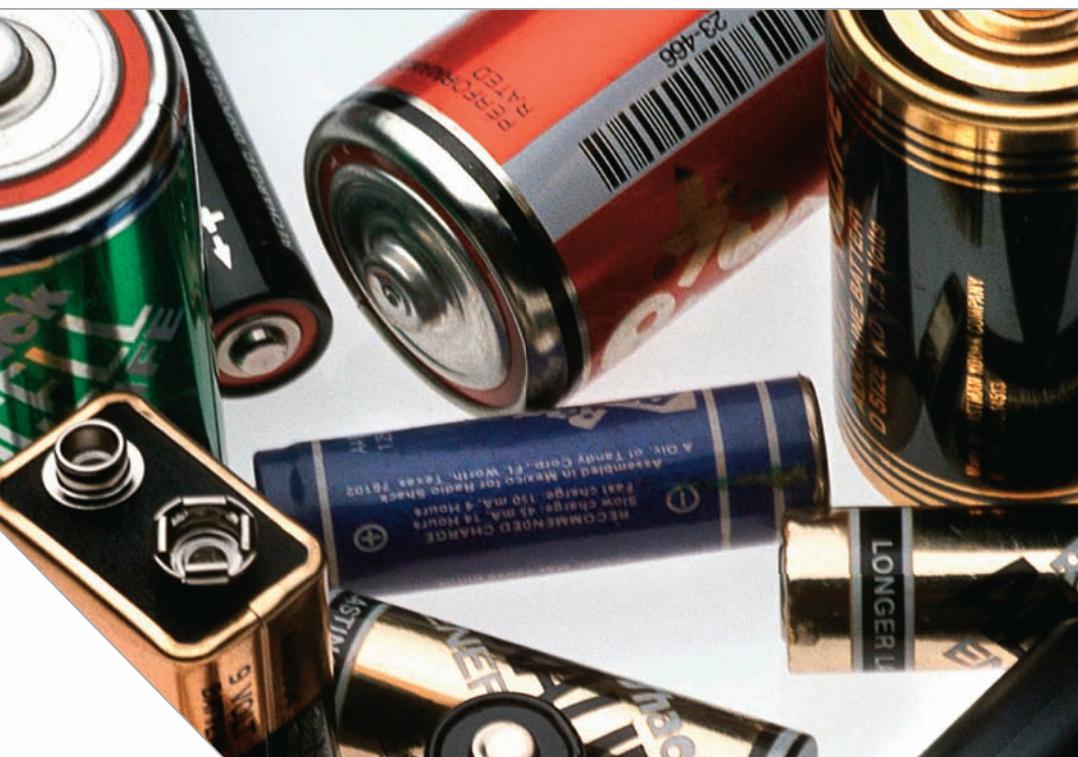
Answers to Practice Exercises

12.1 4.01 **12.2** (a) and (c) **12.3** 9.17, 9.20 **12.4** Weigh out Na₂CO₃ and NaHCO₃ in a mole ratio of 0.60 to 1.0. Dissolve in enough water to make up a 1-L solution. **12.5** (a) 2.19, (b) 3.95, (c) 8.02, (d) 11.39 **12.6** 5.92 **12.7** (a) Bromophenol blue, methyl orange, methyl red, and chlorophenol blue; (b) all except thymol blue, bromophenol blue, and methyl orange; (c) cresol red and phenolphthalein **12.8** (a) insoluble;

(b) insoluble; (c) soluble **12.9** 2.0 × 10⁻¹⁴ **12.10** 1.9 × 10⁻³ g L⁻¹ **12.11** No **12.12** (a) > 1.6 × 10⁻⁹ M, (b) > 2.6 × 10⁻⁶ M **12.13** (a) 1.7 × 10⁻⁴ g L⁻¹, (b) 1.4 × 10⁻⁷ g L⁻¹ **12.14** (a) More soluble in acid solution, (b) more soluble in acid solution, (c) about the same **12.15** Fe(OH)₂ precipitate will form. **12.16** [Cu²⁺] = 1.2 × 10⁻¹³ M, [Cu(NH₃)₄²⁺] = 0.017 M, [NH₃] = 0.23 M **12.17** 3.5 × 10⁻³ mol L⁻¹

13 Chapter

Electrochemistry



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- 13.2** Redox Reactions Can Be Used to Generate Electric Current in a Galvanic Cell 671
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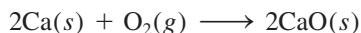
13.1 | Oxidation-Reduction (Redox) Reactions Involve a Transfer of Electrons from One Species to Another

One form of energy that has tremendous practical significance is electric energy. A day without electricity from either the power company or batteries is unimaginable in our technological society. *The branch of chemistry that studies the interconversion of electric energy and chemical energy is called electrochemistry.* Electrochemical processes are **oxidation-reduction reactions** (or **redox reactions**) in which the energy released by a spontaneous reaction is converted to electricity or in which electric energy is used to cause a nonspontaneous reaction to occur. In redox reactions, electrons are transferred from one substance to another. The reaction between magnesium metal and hydrochloric acid is an example of a redox reaction:

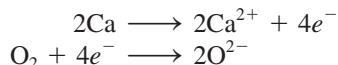


In this reaction, the Mg metal loses two electrons, and the two H⁺ ions in the HCl solution gain one electron each. Species that lose electrons in a redox reaction are said to be **oxidized**, and those that gain electrons are said to be **reduced**. In the reaction of magnesium metal with hydrochloric acid, for example, Mg metal is oxidized and H⁺ ions are reduced. The Cl⁻ ions are *spectator ions* because they do not participate directly in the redox reaction.

Oxidation-reduction reactions are very much a part of the world around us. They range from the burning of fossil fuels to the action of household bleach. Additionally, most metallic and nonmetallic elements are obtained from their ores by the process of oxidation or reduction. Many important redox reactions take place in water (rusting, for example), but not all redox reactions occur in aqueous solution. Some, such as the formation of calcium oxide (CaO) from calcium and oxygen, occur when a solid interacts with a gas:



CaO is an ionic compound made up of Ca²⁺ and O²⁻ ions. In this reaction, two Ca atoms give up or transfer four electrons to two O atoms (in O₂). For convenience, we can think of this process as two separate steps, one involving the loss of four electrons by the two Ca atoms and the other being the gain of four electrons by an O₂ molecule:



In an oxidation half-reaction, electrons appear as product; in a reduction half-reaction, electrons appear as a reactant.

Each of these steps is called a **half-reaction**, and each half-reaction explicitly shows the electrons involved in the oxidation portion or the reduction portion of a redox reaction. The sum of the oxidation half-reaction and the reduction half-reaction gives the overall redox reaction.

An **oxidation reaction** is the half-reaction that involves a loss of electrons. Chemists originally used *oxidation* to denote the combination of elements with oxygen. Now, however, “oxidation” has a broader meaning that includes reactions not involving oxygen. A **reduction reaction** is a half-reaction that involves a gain of electrons. In the formation of calcium oxide, calcium is oxidized. It acts as a **reducing agent** because it *donates electrons* to oxygen and causes oxygen to be reduced. Oxygen is reduced and acts as an **oxidizing agent** because it *accepts electrons* from calcium, causing calcium to be oxidized. An oxidation reaction cannot occur without a concomitant reduction reaction, and vice versa. The number of electrons lost by a reducing agent must equal the number of electrons gained by an oxidizing agent.

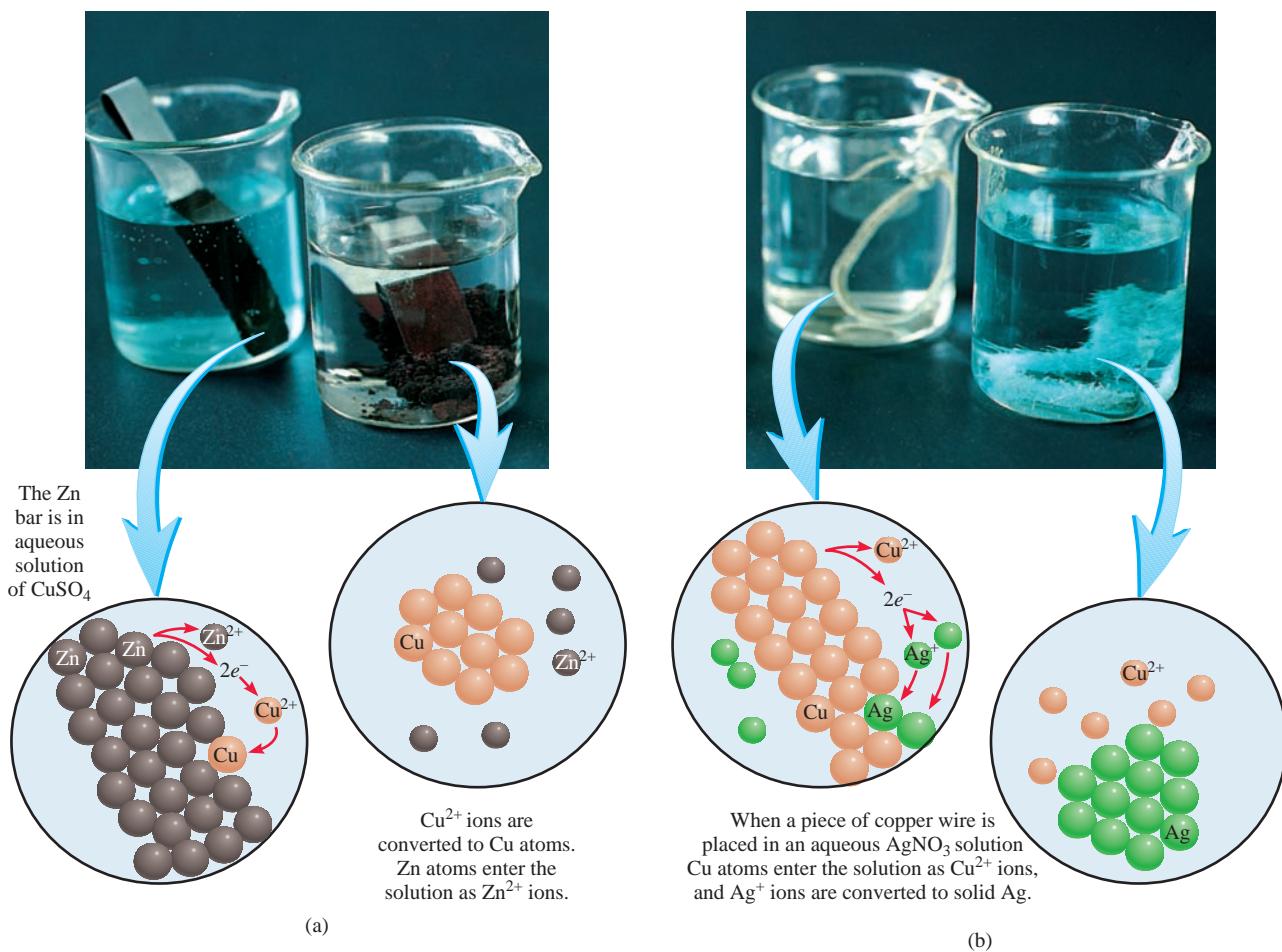


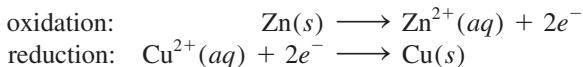
Figure 13.1 Metal displacement reactions in solution. (a) First beaker: A zinc strip is placed in a blue CuSO_4 solution. Immediately Cu^{2+} ions are reduced to metallic Cu in the form of a dark layer. Second beaker: In time, most of the Cu^{2+} ions are reduced and the solution becomes colorless. (b) First beaker: A piece of Cu wire is placed in a colorless AgNO_3 solution. Ag^+ ions are reduced to metallic Ag. Second beaker: As time progresses, most of the Ag^+ ions are reduced, and the solution acquires the characteristic blue color of hydrated Cu^{2+} ions.

When metallic zinc is added to a solution containing copper(II) sulfate (CuSO_4), zinc donates two electrons, thus forming Zn^{2+} and reducing Cu^{2+} to copper metal:

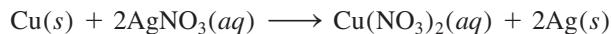


In the process, the solution loses the blue color that is characteristic of hydrated Cu^{2+} ions and copper metal precipitates from the solution (Figure 13.1).

The oxidation and reduction half-reactions are



Similarly, metallic copper reduces silver ions in a solution of silver nitrate (AgNO_3):



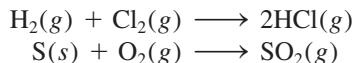
or



The reactions shown in Figure 13.1 are examples of *metal displacement reactions*.

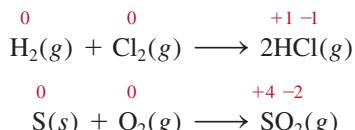
Oxidation Number

Defining oxidation and reduction in terms of the loss and gain of electrons, respectively, works well for the formation of ionic compounds such as CaO or the reduction of Cu²⁺ ions by Zn. These definitions, however, do not accurately characterize the formation of hydrogen chloride (HCl) and sulfur dioxide (SO₂):



Because HCl and SO₂ are molecular compounds (not ionic), no electrons are actually transferred in the formation of these compounds. Nevertheless, chemists find it convenient to treat these reactions as redox reactions because experimental measurements show that there is a partial transfer of electrons (from H to Cl in HCl and from S to O in SO₂).

To keep track of electrons in redox reactions, it is useful to assign *oxidation numbers* to the reactants and products. The ***oxidation number*** of an atom, also called its ***oxidation state***, signifies the *number of charges the atom would have in a molecule (or an ionic compound) if electrons were transferred completely*. For example, the oxidation numbers for the species involved in the formation of HCl and SO₂ (shown above the element symbols) are as follows:



In both of these reactions, the oxidation numbers for the atoms in the reactants are zero because the reactant molecules are pure elements. For the product molecules, however, it is assumed that complete electron transfer has taken place and that atoms have gained or lost electrons.

The oxidation numbers reflect the number of electrons “transferred” and enable us to identify elements that are oxidized and reduced at a glance. The elements that show an increase in oxidation number—hydrogen and sulfur in the preceding examples—are oxidized. The elements that show a decrease in oxidation number—chlorine and oxygen—are reduced. Note that the sum of the oxidation numbers of H and Cl in HCl (+1 and -1) is zero. Likewise, if we add the charges on S (+4) and two atoms of O [2 × (-2)], the total is zero. The totals are zero because the HCl and SO₂ molecules are neutral, so the charges must cancel.

Use the following rules to assign oxidation numbers:

1. In free elements (that is, elements in the uncombined state), each atom has an oxidation number of zero. Thus, each atom in H₂, Br₂, Na, Be, K, O₂, and P₄ has the same oxidation number: zero.
2. For ions composed of only one atom (that is, monatomic ions), the oxidation number is equal to the charge on the ion. Thus, the Li⁺ ion has an oxidation number of +1; Ba²⁺ ion, +2; Fe³⁺ ion, +3; I⁻ ion, -1; O²⁻ ion, -2; and so on. All alkali metals have an oxidation number of +1, and all alkaline earth metals have an oxidation number of +2 in their compounds. Aluminum has an oxidation number of +3 in all its compounds.
3. The oxidation number of oxygen in most compounds (for example, MgO and H₂O) is -2. *Exceptions:* The oxidation number of oxygen in hydrogen peroxide

(H_2O_2) and peroxide ion (O_2^{2-}) is -1 ; in the superoxide anion (O_2^-), it is $-1/2$ (thus, oxidation numbers are generally, but not necessarily, integers).

4. The oxidation number of hydrogen is $+1$. *Exceptions:* When hydrogen is bonded to metals in binary compounds (for example, LiH , NaH , and CaH_2), its oxidation number is -1 .
5. The oxidation number of halogens (F, Cl, Br, and I) is -1 . *Exceptions:* When Cl, Br, and I are bonded to other halogens, only the most electronegative halogen in the bond has an oxidation number of -1 . When combined with oxygen—for example, in oxoacids and oxoanions (see Section 0.3)—Cl, Br, and I have positive oxidation numbers because oxygen is more electronegative.
6. The sum of the oxidation numbers of all the elements in a molecule or polyatomic ion must equal the net charge on the molecule or ion. In a neutral molecule, for example, such as NH_3 , the sum of the oxidation numbers of all the atoms must be zero. The oxidation number of N is -3 and of H is $+1$, so the sum of the oxidation numbers is $-3 + 3(+1) = 0$. For the polyatomic ammonium ion, NH_4^+ , the oxidation numbers of N and H are still -3 and $+1$, respectively. The sum of the oxidation numbers, however, is $-3 + 4(+1) = +1$, which is equal to the net charge on the ion.

Example 13.1 shows how to apply these rules to assign oxidation numbers to neutral and charged species.

Example 13.1

Assign oxidation numbers to all the elements in the following compounds and ion: (a) Li_2O , (b) HNO_3 , (c) $\text{Cr}_2\text{O}_7^{2-}$, and (d) ClF_3 .

Strategy Use the rules for assigning oxidation numbers. All alkali metals have an oxidation number of $+1$, and in most cases hydrogen has an oxidation number of $+1$ and oxygen has an oxidation number of -2 in their compounds. Fluorine, the most electronegative element, has an oxidation number of -1 (except in F_2 , where its oxidation number is 0).

- Solution** (a) According to rule 2, lithium has an oxidation number of $+1$ (Li^+) and oxygen has an oxidation number of -2 (O^{2-}).
(b) This is the formula for nitric acid, which yields an H^+ ion and an NO_3^- ion in solution. According to rule 4, H^+ has an oxidation number of $+1$, and according to rule 6, the nitrate ion must have a net oxidation number of -1 . Oxygen has an oxidation number of -2 (rule 3), and if we use x to represent the oxidation number of nitrogen, then $x + 3(-2) = -1$ or $x = 5$.
(c) According to rule 6, the sum of the oxidation numbers in the dichromate ion $\text{Cr}_2\text{O}_7^{2-}$ must be -2 . The oxidation number of O is -2 (rule 3), so we can determine the oxidation number of Cr by setting it equal to y : $2(y) + 7(-2) = -2$ or $y = 6$.
(d) In ClF_3 the three F atoms are bonded to the less electronegative Cl atom, which has an expanded octet. According to rule 5, each F has an oxidation number of -1 . Because the overall molecule is neutral, the Cl atom must have an oxidation number of $+3$ so that the oxidation numbers sum to zero [$+3 + 3(-1) = 0$].

Check In each case, does the sum of the oxidation numbers of all the atoms equal the net charge on the species?

Practice Exercise Assign oxidation numbers to all the elements in the following compound and ion: (a) PF_3 , (b) MnO_4^- , (c) ClO_3^- , and (d) SF_6 .

| | | | | | | | | | | | | | | | | | | |
|--------------------------|---------------------|---------------------|----------------------------------|---------------------------------------|--|---|---|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------------|----------------------------|--|--|--|---------|
| 1 1A H +1 -1 | 2 2A Be +2 | 3 3B Li +1 | 4 4B Sc +3 | 5 5B Ti +4 +5 +3 +2 | 6 6B V +5 +6 +4 +3 +2 | 7 7B Cr +6 +7 +5 +4 +3 +2 | 8 8B Mn +7 +6 +5 +4 +3 +2 | 9 Fe +3 +2 +1 | 10 Co +3 +2 +1 | 11 1B Ni +2 +1 | 12 2B Cu +2 +1 | 13 3A Zn +2 | 14 4A Ga +3 | 15 5A Ge +4 -4 | 16 6A As +5 +4 +3 -3 | 17 7A Se +6 +5 +4 +3 -1 | 18 8A Br +5 +4 +3 +2 -1 | 2 He |
| 19 K +1 | 20 Ca +2 | 21 Sc +3 | 22 Ti +4 +5 +3 +2 | 23 V +5 +6 +4 +3 +2 | 24 Cr +6 +7 +5 +4 +3 +2 | 25 Mn +7 +6 +5 +4 +3 +2 | 26 Fe +3 +2 | 27 Co +3 +2 | 28 Ni +2 | 29 Cu +2 +1 | 30 Zn +2 | 31 Ga +3 | 32 Ge +4 -4 | 33 As +5 +4 -3 | 34 Se +6 +5 +4 -2 | 35 Br +5 +4 +3 +1 -1 | 36 Kr +4 +2 | |
| 37 Rb +1 | 38 Sr +2 | 39 Y +3 | 40 Zr +4 | 41 Nb +5 +4 | 42 Mo +6 +5 +4 +3 | 43 Tc +7 +6 +5 +4 | 44 Ru +8 +7 +6 +5 +4 +3 | 45 Rh +4 +3 +2 | 46 Pd +4 +2 | 47 Ag +1 | 48 Cd +2 | 49 In +3 +2 | 50 Sn +4 +3 +2 -3 | 51 Sb +5 +4 -2 | 52 Te +6 +5 +4 -2 | 53 I +7 +5 +4 -1 | 54 Xe +6 +5 +4 +2 | |
| 55 Cs +1 | 56 Ba +2 | 57 La +3 | 72 Hf +4 | 73 Ta +5 +4 | 74 W +6 +5 +4 | 75 Re +7 +6 +5 +4 | 76 Os +8 +7 +6 +5 +4 | 77 Ir +4 +3 | 78 Pt +4 +2 | 79 Au +3 +2 +1 | 80 Hg +2 +1 | 81 Tl +3 +2 +1 | 82 Pb +4 +2 | 83 Bi +5 +4 +3 | 84 Po +2 | 85 At -1 | 86 Rn | |

Figure 13.2 The oxidation numbers of elements in their compounds. The more common oxidation numbers are in red.

Figure 13.2 shows the known oxidation numbers of the familiar elements, arranged according to their positions in the periodic table. We can summarize these data as follows:

- ▶ Metallic elements have only positive oxidation numbers, whereas nonmetallic elements may have either positive or negative oxidation numbers.
- ▶ The highest oxidation number an element in groups 1A–7A can have is its group number. For example, the halogens are in group 7A, so their highest possible oxidation number is +7.
- ▶ The transition metals (groups 1B and 3B–8B) usually have several possible oxidation numbers.

Balancing Redox Equations

Equations for redox reactions, such as the oxidation of magnesium metal by chlorine gas discussed at the beginning of this section, are relatively straightforward to balance. In the laboratory, however, we often encounter more complex redox reactions involving oxoanions such as chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), permanganate (MnO_4^-),

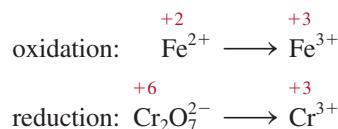
nitrate (NO_3^-), and sulfate (SO_4^{2-}). In principle, we can balance any redox equation using the procedure outlined in Section 0.4, but there are some special techniques for handling redox reactions, techniques that also give us insight into electron transfer processes. We will discuss one such procedure here, called the *ion-electron method*. In this approach, the overall reaction is divided into two half-reactions, one for oxidation and one for reduction. The equations for the two half-reactions are balanced separately and then added together to give the overall balanced equation.

Suppose, for example, that we are asked to balance the equation for the oxidation of Fe^{2+} ions to Fe^{3+} ions by dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$) in an acidic medium. In this reaction, the $\text{Cr}_2\text{O}_7^{2-}$ ions are reduced to Cr^{3+} ions. The following steps will help us balance the equation by the ion-electron method.

Step 1: Write the unbalanced equation for the reaction in ionic form.

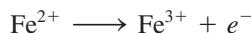


Step 2: Separate the equation into two half-reactions.

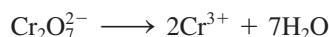


Step 3: Balance each half-reaction for number and type of atoms and charges. For reactions in an acidic medium, add H_2O to balance the O atoms and H^+ to balance the H atoms.

Oxidation half-reaction: The atoms are already balanced. To balance the charge, we add an electron to the right-hand side of the arrow:



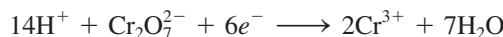
Reduction half-reaction: Because the reaction takes place in an acidic medium, we add seven H_2O molecules to the right-hand side of the arrow to balance the O atoms:



To balance the H atoms, we add 14 H^+ ions to the left-hand side:

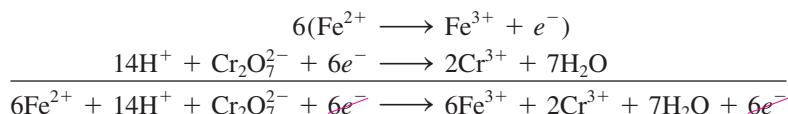


There are now 12 positive charges on the left-hand side and only 6 positive charges on the right-hand side. Therefore, we add six electrons on the left:



Step 4: Add the two half-reactions together, and balance the final equation by inspection. The electrons on both sides must cancel. If the oxidation and reduction half-reactions contain different numbers of electrons, we need to multiply one or both half-reactions by a coefficient to equalize the number of electrons.

Here we have only one electron for the oxidation half-reaction and six electrons for the reduction half-reaction, so we need to multiply the oxidation half-reaction by 6:



The electrons on both sides cancel, and we are left with the balanced net ionic equation:



Step 5: Verify that the equation contains the same type and numbers of atoms and the same total charge on both sides of the equation.

There are 6 Fe, 14 H, 2 Cr, and 7 O on both sides of the equation, and the charge on both sides is +24. The resulting equation, therefore, is “atomically” and “electrically” balanced.

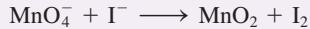
For reactions in a basic medium, we proceed through step 4 as if the reaction were carried out in an acidic medium. Then, for every H^+ ion we add an equal number of OH^- ions to *both* sides of the equation. Where H^+ and OH^- ions appear on the same side of the equation, we combine the ions to give H_2O . Example 13.2 illustrates this procedure.

Example 13.2

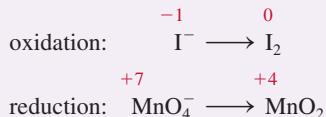
Write a balanced equation for the oxidation of iodide ion (I^-) by permanganate ion (MnO_4^-) in basic solution to yield molecular iodine (I_2) and manganese(IV) oxide (MnO_2).

Strategy Follow the procedure for balancing redox equations by the ion-electron method. The reaction takes place in a basic medium, so any H^+ ions that appear in the two half-reactions must be neutralized by adding an equal number of OH^- ions to both sides of the equation.

Solution *Step 1:* The unbalanced equation is



Step 2: The two half-reactions are



Step 3: Balance each half-reaction for the number and type of atoms and charges.

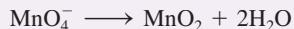
For the oxidation half-reaction, we first balance the number of iodine atoms:



To balance charges, add two electrons to the right-hand side of the equation:



For the reduction half-reaction, we balance the O atoms by adding two H_2O molecules on the right-hand side:



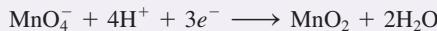
To balance the H atoms, add four H^+ ions on the left-hand side:



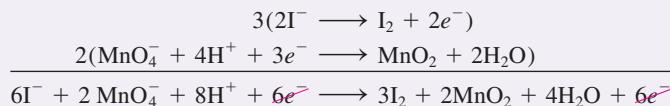
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Continued—

There are three net positive charges on the left, so add three electrons to the same side to balance the charges:



Step 4: Add the oxidation and reduction half-reactions to give the overall reaction. In order to equalize the number of electrons, multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2:



The electrons on both sides cancel, and we are left with the balanced net ionic equation:



This is the balanced equation in an *acidic* medium, but the reaction is carried out in a *basic* medium. Thus, for every H^+ ion, we need to add an equal number of OH^- ions to *both* sides of the equation:



Finally, combining the H^+ and OH^- ions to form water, we obtain



Step 5: A final check shows that the equation is balanced in terms of both atoms and charges. There are 6 I, 2 Mn, 12 O, and 8 H atoms on both sides of the equation, and the charge on both sides is -8 .

Practice Exercise Use the ion-electron method to balance the following equation for the reaction in an acidic medium:



13.2 | Redox Reactions Can Be Used to Generate Electric Current in a Galvanic Cell

We saw in Section 13.1 that when a piece of zinc metal is placed in a CuSO_4 solution, Zn is oxidized to Zn^{2+} ions whereas Cu^{2+} ions are reduced to metallic copper (see Figure 13.1):



The electrons are transferred directly from the reducing agent (Zn) to the oxidizing agent (Cu^{2+}) in solution. However, if we physically separate the oxidizing agent from the reducing agent, the transfer of electrons can take place via an external conducting medium (a metal wire). As the reaction progresses, it sets up a constant flow of electrons and hence generates an electric current. The electric work produced by the current can be used to drive an electric motor or to operate a lightbulb.

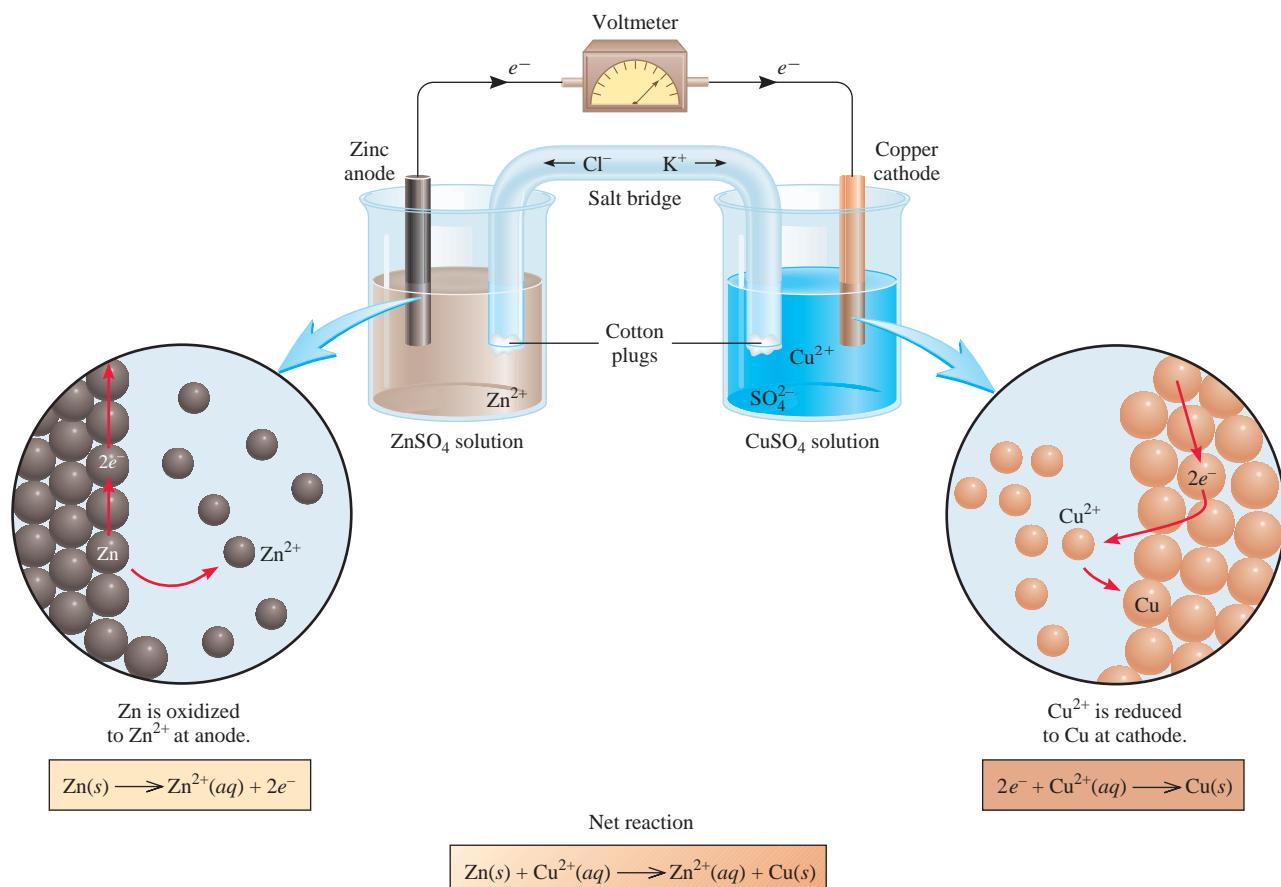


Figure 13.3 A galvanic cell. The salt bridge (an inverted U-shaped tube) containing a KCl solution provides an electrically conducting medium between the two solutions. The openings of the U-shaped tube are loosely plugged with cotton balls to prevent the KCl solution from flowing into the containers while allowing the anions and cations to move across. Electrons flow externally from the Zn electrode (anode) to the Cu electrode (cathode).

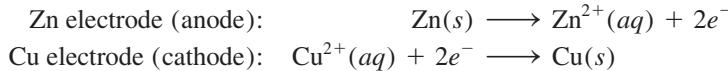
The experimental apparatus for generating electric current through the use of a spontaneous reaction is called a **galvanic cell** or **voltaic cell**, after the Italian scientists Luigi Galvani¹ and Alessandro Volta,² who constructed early versions of the device. Figure 13.3 shows the essential components of a galvanic cell. A zinc bar is immersed in a ZnSO₄ solution, and a copper bar is immersed in a CuSO₄ solution. The cell operates on the principle that the oxidation of Zn to Zn²⁺ and the reduction of Cu²⁺ to Cu can be made to take place simultaneously in separate locations with the transfer of electrons between them occurring through an external wire. The zinc and copper bars are called **electrodes**. This particular arrangement of electrodes (Zn and Cu) and solutions (ZnSO₄ and CuSO₄) is called the Daniell cell

1. Luigi Galvani (1737–1798). Italian biologist and physician. Galvani discovered that external electric impulses (sparks) applied to the leg muscles of a frog could make the muscles twitch (contract rapidly) even when the legs were detached from the body. His discoveries formed the basis for the science of neurology. Galvani's work provided much of the background and motivation for Volta's invention of the electric pile (battery).

2. Count Alessandro Giuseppe Antonio Anastasio Volta (1745–1827). Italian physicist. Volta showed that animal tissue was not necessary for the conduction of electricity, as had been hypothesized by Galvani. He invented the first electric (or voltaic) pile—a prototype battery consisting of alternating discs of dissimilar metals (for example, copper and zinc) separated by cardboard soaked in saltwater.

after the English chemist John Frederic Daniell.³ By definition, the **anode** in a galvanic cell is *the electrode at which oxidation occurs* and the **cathode** is *the electrode at which reduction occurs*.

For the Daniell cell, the **half-cell reactions** (that is, *the oxidation and reduction reactions at the electrodes*) are



Unless the two solutions are separated from each other, the Cu^{2+} ions will react directly with the zinc bar:



and no useful electric work will be obtained.

To complete the electric circuit, the solutions must be connected by a conducting medium through which cations and anions can move from one electrode compartment to the other. This requirement is satisfied by a *salt bridge*, which, in its simplest form, is an inverted U-shaped tube containing an inert electrolyte solution, such as KCl or NH_4NO_3 , whose ions will not react with other ions in solution or with the electrodes (see Figure 13.3). During the course of the overall redox reaction, electrons flow externally from the anode (Zn electrode) through the wire and voltmeter to the cathode (Cu electrode). In the solution, the cations (Zn^{2+} , Cu^{2+} , and K^+) move toward the cathode, while the anions (SO_4^{2-} and Cl^-) move toward the anode. Without the salt bridge connecting the two solutions, the buildup of positive charge in the anode compartment (due to the formation of Zn^{2+} ions) and the buildup of negative charge in the cathode compartment (created when the Cu^{2+} ions are reduced to Cu) would quickly prevent the cell from operating.

An electric current flows from the anode to the cathode because there is a difference in electric potential energy between the electrodes. This flow of electric current is analogous to that of water over a waterfall, which occurs because there is a difference in gravitational potential energy between the top and bottom, or the flow of gas from a high-pressure region to a low-pressure region. Experimentally the *difference in electric potential between the anode and the cathode* is measured by a voltmeter (Figure 13.4) and the reading (in volts) is called **cell voltage** or **cell potential**. In the limit that the cell is operated reversibly,⁴ the cell voltage is referred to as the **electromotive force** or **emf** (\mathcal{E}). We will see that the voltage of a cell depends not only on the nature of the electrodes and the ions, but also on the concentrations of the ions and the temperature at which the cell is operated.

The conventional notation for representing galvanic cells is the **cell diagram**. The cell diagram for the Daniell cell shown in Figure 13.3, assuming that the concentrations of Zn^{2+} and Cu^{2+} ions are in their standard states (1 M, if the solutions can be approximated as ideal), is as follows:



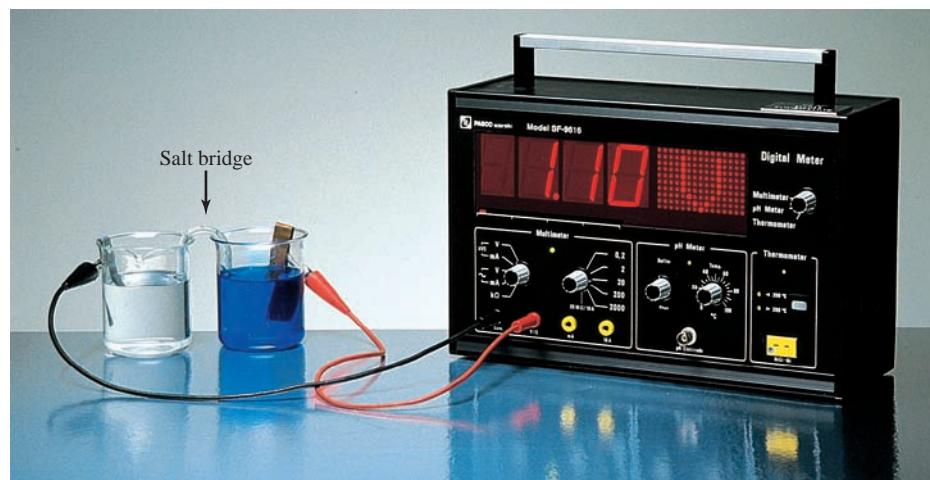
A useful mnemonic device to remember that oxidation occurs at the anode and reduction occurs at the cathode is to note that both **anode** and **oxidation** begin with vowels and both **cathode** and **reduction** begin with consonants.

Half-cell reactions are similar to the half-reactions discussed earlier.

3. John Frederic Daniell (1790–1845). English chemist and meteorologist. In addition to invention of the Daniell cell, an improvement over Volta's electric pile, Daniell made contributions to instrumental meteorology through his invention of a dew-point hygrometer that became a standard instrument for measuring relative humidity.

4. A cell is operated reversibly when a sufficiently large countervoltage is applied to the cell to make the net current go to zero. The electromotive force is then equal to the negative of this counter voltage. Because of the second law of thermodynamics, the cell voltage of a real cell will be greater than the electromotive force.

Figure 13.4 Practical setup of the galvanic cell described in Figure 13.3. Note the U-shaped tube (salt bridge) connecting the two beakers. When the aqueous solutions of ZnSO_4 and CuSO_4 are in their standard states at 25°C , the cell voltage is 1.10 V.



The single vertical line represents a phase boundary. The zinc electrode, for example, is a solid and the Zn^{2+} ions (from ZnSO_4) are in solution. Thus, we draw a line between Zn and Zn^{2+} to show the phase boundary. The double vertical lines denote the salt bridge. By convention, the anode is written first, to the left of the double lines, and the other components appear in the order in which we would encounter them in moving from the anode to the cathode.

13.3 The Standard Emf of Any Electrochemical Cell Can Be Determined If the Standard Reduction Potentials for the Half-Reactions Are Known

Recall that the *emf* is the cell voltage when the cell is operated reversibly.

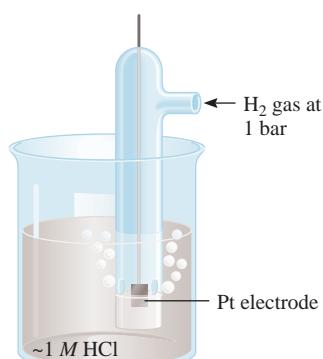


Figure 13.5 A hydrogen electrode operating under standard-state conditions. Hydrogen gas at 1 bar is bubbled through a HCl solution in which the H^+ activity is 1 (approximately 1 M). The platinum electrode is part of the hydrogen electrode.

When the Cu^{2+} and Zn^{2+} ions are in their standard states (that is, both have an activity of 1 in the solution), we find that the emf of a Daniell cell is 1.10 V at 25°C (see Figure 13.4). This emf must be related directly to the redox reactions, but how? Just as the overall cell reaction can be thought of as the sum of two half-cell reactions, the measured emf of the cell can be treated as the sum of the electric potentials at the Zn and Cu electrodes. Knowing one of these electrode potentials, we could obtain the other by subtraction (from 1.10 V). It is impossible to measure the potential of just a single electrode, but if we arbitrarily set the potential value of a particular electrode at zero, we can use it to determine the relative potentials of other electrodes. The hydrogen electrode, shown in Figure 13.5, serves as the reference for this purpose.

Hydrogen gas is bubbled into a hydrochloric acid solution at 25°C . The platinum electrode has two functions. First, it provides a surface on which the dissociation of hydrogen molecules can take place:



Second, it serves as an electric conductor to the external circuit. Under standard-state conditions [when the pressure of $\text{H}_2(g)$ is 1 bar and the activity of H^+ is unity in the solution], the potential for the reduction of H^+ at 25°C is taken to be *exactly* zero:



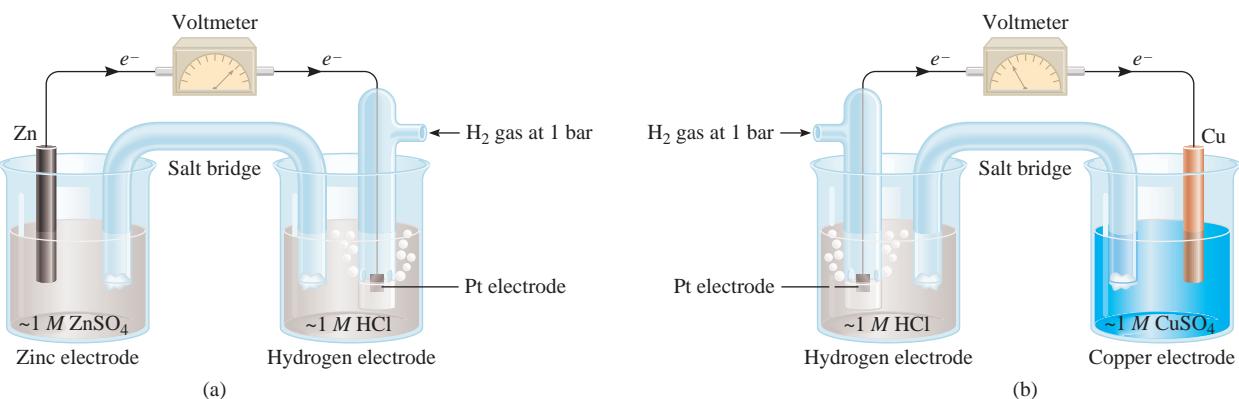


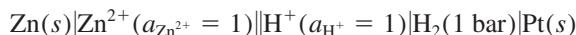
Figure 13.6 (a) A cell consisting of a zinc electrode and a hydrogen electrode. (b) A cell consisting of a copper electrode and a hydrogen electrode. Both cells are operating under standard-state conditions [unit activities ($\sim 1\text{ M}$) for ions, $P = 1\text{ bar}$ for gases]. Note that in part (a) the standard hydrogen electrode acts as the cathode, but in part (b), it is the anode.

The superscript “ $^\circ$ ” denotes standard-state conditions, and E° is the **standard reduction potential**, or the electromotive force associated with a reduction reaction at an electrode when reactant and product species are in their standard states. Thus, the standard reduction potential of the hydrogen electrode is defined as zero. The hydrogen electrode is called the **standard hydrogen electrode (SHE)**.

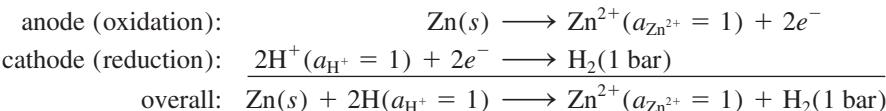
We can use the standard hydrogen electrode to measure the potentials of other kinds of electrodes. For example, Figure 13.6(a) shows a galvanic cell with a zinc electrode and a standard hydrogen electrode. In this case the zinc electrode is the anode and the standard hydrogen electrode is the cathode. We deduce this fact from the decrease in mass of the zinc electrode during the operation of the cell, which is consistent with the loss of zinc to the solution caused by the oxidation reaction:



The cell diagram is



As mentioned earlier, the Pt electrode provides the surface on which the reduction takes place. When all the reactants are in their standard states (i.e., H_2 at 1 bar, H^+ and Zn^{2+} ions at unit activity), the emf of the cell is measured to be 0.76 V at 25°C. We can write the half-cell reactions as follows:



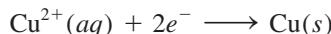
By convention, the **standard emf** of the cell, E_{cell}° , which is composed of a contribution from the anode and a contribution from the cathode, is given by

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \quad (13.1)$$

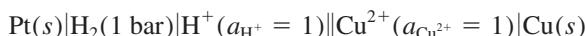
where both E_{cathode}° and E_{anode}° are the standard reduction potentials of the electrodes. For the Zn-SHE cell, we write

$$E_{\text{cell}}^\circ = E_{\text{H}^+|\text{H}_2}^\circ - E_{\text{Zn}^{2+}|\text{Zn}}^\circ = 0\text{ V} - 0.76\text{ V} = -0.76\text{ V}$$

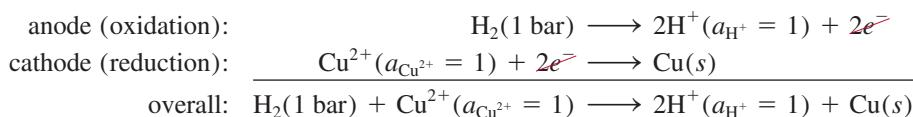
where the subscript $\text{H}^+|\text{H}_2$ denote $2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$ and the subscript $\text{Zn}^{2+}|\text{Zn}$ denotes $\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$. Thus, the standard reduction potential of zinc ($E_{\text{Zn}^{2+}|\text{Zn}}^\circ$) is -0.76 V. The standard electrode potential of copper can be obtained in a similar fashion, by using a cell with a copper electrode and a standard hydrogen electrode [Figure 13.6(b)]. In this case, the copper electrode is the cathode because its mass increases during the operation of the cell, as is consistent with the reduction reaction:



The cell diagram is



and the half-cell reactions are

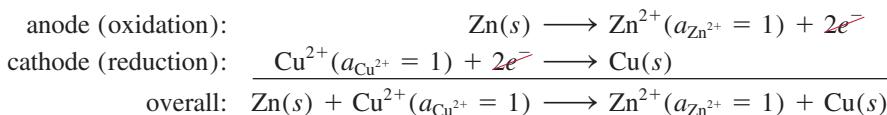


Under standard-state conditions and at 25°C , the emf of the cell is 0.34 V, so we write

$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ 0.34 \text{ V} &= E_{\text{Cu}^{2+}|\text{Cu}}^\circ - E_{\text{H}^+|\text{H}_2}^\circ \\ &= E_{\text{Cu}^{2+}|\text{Cu}}^\circ - 0 \text{ V} \end{aligned}$$

In this case, the standard reduction potential of copper, $E_{\text{Cu}^{2+}|\text{Cu}}^\circ$, is $+0.34$ V, where the subscript denotes $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$.

For the Daniell cell shown in Figure 13.3, we can now write



The emf of the cell is

$$\begin{aligned} E_{\text{cell}}^\circ &= E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ \\ &= E_{\text{Cu}^{2+}|\text{Cu}}^\circ - E_{\text{Zn}^{2+}|\text{Zn}}^\circ \\ &= +0.34 \text{ V} - (-0.76 \text{ V}) \\ &= +1.10 \text{ V} \end{aligned}$$

As in the case of ΔG° (page 533), we can use the sign of E_{cell}° to predict the extent of a redox reaction. A positive E_{cell}° means the redox reaction will favor the formation of products at equilibrium. Conversely, a negative E_{cell}° means that more reactants than products will be formed at equilibrium. We will examine the relationships among E_{cell}° , ΔG° , and K later in Section 13.4.

Table 13.1 lists standard reduction potentials for a number of half-cell reactions. By definition, the SHE has an E° value of 0.00 V. Below the SHE, the negative standard reduction potentials increase, and above it, the positive standard reduction potentials increase.

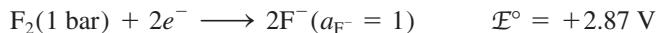
Table 13.1 Standard Reduction Potentials at 25°C*

| Half-Reaction | $E^\circ(V)$ |
|--|--------------|
| $\text{F}_2(g) + 2e^- \longrightarrow 2\text{F}^-(aq)$ | +2.87 |
| $\text{O}_3(g) + 2\text{H}^+(aq) + 2e^- \longrightarrow \text{O}_2(g) + \text{H}_2\text{O}$ | +2.07 |
| $\text{Co}^{3+}(aq) + e^- \longrightarrow \text{Co}^{2+}(aq)$ | +1.82 |
| $\text{H}_2\text{O}_2(aq) + 2\text{H}^+(aq) + 2e^- \longrightarrow 2\text{H}_2\text{O}$ | +1.77 |
| $\text{PbO}_2(s) + 4\text{H}^+(aq) + \text{SO}_4^{2-}(aq) + 2e^- \longrightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}$ | +1.70 |
| $\text{Ce}^{4+}(aq) + e^- \longrightarrow \text{Ce}^{3+}(aq)$ | +1.61 |
| $\text{MnO}_4^-(aq) + 8\text{H}^+(aq) + 5e^- \longrightarrow \text{Mn}^{2+}(aq) + 4\text{H}_2\text{O}$ | +1.51 |
| $\text{Au}^{3+}(aq) + 3e^- \longrightarrow \text{Au}(s)$ | +1.50 |
| $\text{Cl}_2(g) + 2e^- \longrightarrow 2\text{Cl}^-(aq)$ | +1.36 |
| $\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^- \longrightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}$ | +1.33 |
| $\text{MnO}_2(s) + 4\text{H}^+(aq) + 2e^- \longrightarrow \text{Mn}^{2+}(aq) + 2\text{H}_2\text{O}$ | +1.23 |
| $\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \longrightarrow 2\text{H}_2\text{O}$ | +1.23 |
| $\text{Br}_2(l) + 2e^- \longrightarrow 2\text{Br}^-(aq)$ | +1.07 |
| $\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \longrightarrow \text{NO}(g) + 2\text{H}_2\text{O}$ | +0.96 |
| $2\text{Hg}^{2+}(aq) + 2e^- \longrightarrow \text{Hg}_2^{2+}(aq)$ | +0.92 |
| $\text{Hg}_2^{2+}(aq) + 2e^- \longrightarrow 2\text{Hg}(l)$ | +0.85 |
| $\text{Ag}^+(aq) + e^- \longrightarrow \text{Ag}(s)$ | +0.80 |
| $\text{Fe}^{3+}(aq) + e^- \longrightarrow \text{Fe}^{2+}(aq)$ | +0.77 |
| $\text{O}_2(g) + 2\text{H}^+(aq) + 2e^- \longrightarrow \text{H}_2\text{O}_2(aq)$ | +0.68 |
| $\text{MnO}_4^-(aq) + 2\text{H}_2\text{O} + 3e^- \longrightarrow \text{MnO}_2(s) + 4\text{OH}^-(aq)$ | +0.59 |
| $\text{I}_2(s) + 2e^- \longrightarrow 2\text{I}^-(aq)$ | +0.53 |
| $\text{O}_2(g) + 2\text{H}_2\text{O} + 4e^- \longrightarrow 4\text{OH}^-(aq)$ | +0.40 |
| $\text{Cu}^{2+}(aq) + 2e^- \longrightarrow \text{Cu}(s)$ | +0.34 |
| $\text{AgCl}(s) + e^- \longrightarrow \text{Ag}(s) + \text{Cl}^-(aq)$ | +0.22 |
| $\text{SO}_4^{2-}(aq) + 4\text{H}^+(aq) + 2e^- \longrightarrow \text{SO}_2(g) + 2\text{H}_2\text{O}$ | +0.20 |
| $\text{Cu}^{2+}(aq) + e^- \longrightarrow \text{Cu}^+(aq)$ | +0.15 |
| $\text{Sn}^{4+}(aq) + 2e^- \longrightarrow \text{Sn}^{2+}(aq)$ | +0.13 |
| $2\text{H}^+(aq) + 2e^- \longrightarrow \text{H}_2(g)$ | 0.00 |
| $\text{Pb}^{2+}(aq) + 2e^- \longrightarrow \text{Pb}(s)$ | -0.13 |
| $\text{Sn}^{2+}(aq) + 2e^- \longrightarrow \text{Sn}(s)$ | -0.14 |
| $\text{Ni}^{2+}(aq) + 2e^- \longrightarrow \text{Ni}(s)$ | -0.25 |
| $\text{Co}^{2+}(aq) + 2e^- \longrightarrow \text{Co}(s)$ | -0.28 |
| $\text{PbSO}_4(s) + 2e^- \longrightarrow \text{Pb}(s) + \text{SO}_4^{2-}(aq)$ | -0.31 |
| $\text{Cd}^{2+}(aq) + 2e^- \longrightarrow \text{Cd}(s)$ | -0.40 |
| $\text{Fe}^{2+}(aq) + 2e^- \longrightarrow \text{Fe}(s)$ | -0.44 |
| $\text{Cr}^{3+}(aq) + 3e^- \longrightarrow \text{Cr}(s)$ | -0.74 |
| $\text{Zn}^{2+}(aq) + 2e^- \longrightarrow \text{Zn}(s)$ | -0.76 |
| $2\text{H}_2\text{O} + 2e^- \longrightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$ | -0.83 |
| $\text{Mn}^{2+}(aq) + 2e^- \longrightarrow \text{Mn}(s)$ | -1.18 |
| $\text{Al}^{3+}(aq) + 3e^- \longrightarrow \text{Al}(s)$ | -1.66 |
| $\text{Be}^{2+}(aq) + 2e^- \longrightarrow \text{Be}(s)$ | -1.85 |
| $\text{Mg}^{2+}(aq) + 2e^- \longrightarrow \text{Mg}(s)$ | -2.37 |
| $\text{Na}^+(aq) + e^- \longrightarrow \text{Na}(s)$ | -2.71 |
| $\text{Ca}^{2+}(aq) + 2e^- \longrightarrow \text{Ca}(s)$ | -2.87 |
| $\text{Sr}^{2+}(aq) + 2e^- \longrightarrow \text{Sr}(s)$ | -2.89 |
| $\text{Ba}^{2+}(aq) + 2e^- \longrightarrow \text{Ba}(s)$ | -2.90 |
| $\text{K}^+(aq) + e^- \longrightarrow \text{K}(s)$ | -2.93 |
| $\text{Li}^+(aq) + e^- \longrightarrow \text{Li}(s)$ | -3.05 |

*For all half-reactions the activity is unity for dissolved species (~1 M) and the pressure is 1 bar for gases. These are the standard-state values.

It is important to know the following points about the table in calculations:

1. The \mathcal{E}° values apply to the half-cell reactions as read in the forward (left to right) direction.
2. The more positive \mathcal{E}° is, the greater the tendency for the substance to be reduced. For example, the half-cell reaction

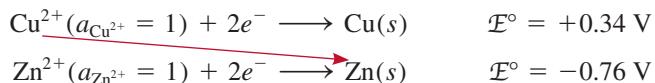


has the highest positive \mathcal{E}° value among all the half-cell reactions. Thus, F_2 is the *strongest* oxidizing agent because it has the greatest tendency to be reduced. At the other extreme is the reaction



which has the most negative \mathcal{E}° value. Thus, Li is the *weakest* oxidizing agent because it is the most difficult species to reduce. Conversely, we say that F^- is the weakest reducing agent and Li metal is the strongest reducing agent. Under standard-state conditions, oxidizing agents (the species on the left-hand side of the half-reactions in Table 13.1) increase in strength from bottom to top and the reducing agents (the species on the right-hand side of the half-reactions) increase in strength from top to bottom.

3. The half-cell reactions are reversible. Depending on the conditions, any electrode can act either as an anode or as a cathode. Earlier we saw that the standard hydrogen electrode is the cathode (H^+ is reduced to H_2) when coupled with zinc in a cell and that it becomes the anode (H_2 is oxidized to H^+) when used in a cell with copper.
4. Under standard-state conditions, any species on the left of a given half-cell reaction will react spontaneously with a species that appears on the right of any half-cell reaction located *below* it in Table 13.1. This principle is sometimes called the *diagonal rule*. In the case of the Daniell cell

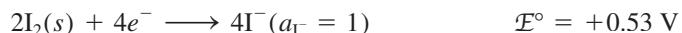


We see that the substance on the left of the first half-cell reaction is Cu^{2+} and the substance on the right in the second half-cell reaction is Zn. Therefore, as we saw earlier, Zn spontaneously reduces Cu^{2+} to form Zn^{2+} and Cu.

5. Changing the stoichiometric coefficients of a half-cell reaction *does not* affect the value of \mathcal{E}° because electrode potentials are intensive properties. This means that the value of \mathcal{E}° is unaffected by the size of the electrodes or the amount of solutions present. For example,



but \mathcal{E}° does not change if we multiply the half-reaction by 2:



6. Like ΔH , ΔG , and ΔS , the sign of \mathcal{E}° changes, but its magnitude remains the same when we reverse a reaction.

As Examples 13.3 and 13.4 show, Table 13.1 enables us to predict the outcome of redox reactions under standard-state conditions, whether they take place in a

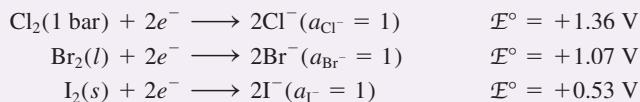
galvanic cell, where the reducing agent and oxidizing agent are physically separated from each other, or in a beaker, where the reactants are all mixed together.

Example 13.3

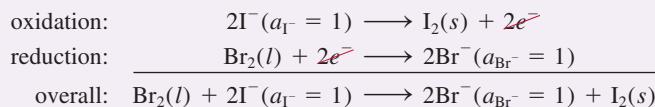
Predict what will happen if molecular bromine (Br_2) is added to a solution containing NaCl and NaI at 25°C . Assume all the species are in their standard states.

Strategy To predict what redox reaction(s) will take place, we need to compare the standard reduction potentials of Cl_2 , Br_2 , and I_2 and apply the diagonal rule.

Solution From Table 13.1, we write the standard reduction potentials as follows:



Applying the diagonal rule, we see that Br_2 will oxidize I^- but will not oxidize Cl^- . Therefore, the only redox reaction that will occur appreciably under standard-state conditions is



Check We can confirm our conclusion by calculating E_{cell}° . Try it. Note that the Na^+ ions are inert and do not enter into the redox reaction.

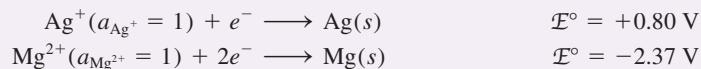
Practice Exercise Can Sn reduce $\text{Zn}^{2+}(aq)$ under standard-state conditions?

Example 13.4

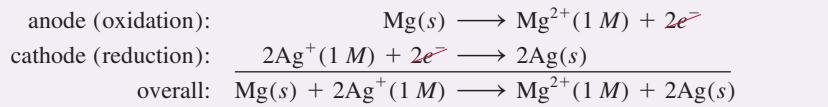
A galvanic cell consists of an Mg electrode in a 1.0 M $\text{Mg}(\text{NO}_3)_2$ solution and an Ag electrode in a 1.0 M AgNO_3 solution. Calculate the standard emf of this cell at 25°C . Assume ideal dilute solutions, that is, the activities of the ions in solution are approximated by M/M° , where $M^\circ = 1 \text{ mol L}^{-1}$.

Strategy At first it may not be clear how to assign the electrodes in the galvanic cell. From Table 13.1, we write the standard reduction potentials of Ag^+ and Mg^{2+} and apply the diagonal rule to determine which is the anode and which is the cathode.

Solution The standard reduction potentials are



Applying the diagonal rule, we see that Ag will oxidize Mg:



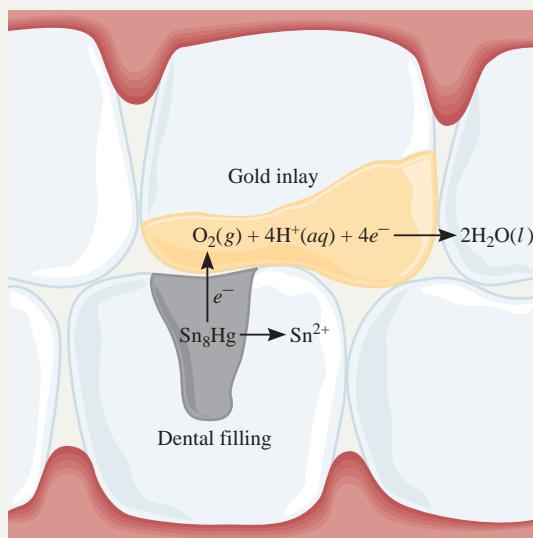
—Continued

Dental Filling Discomfort

In modern dentistry, the material most commonly used to fill decaying teeth is known as *dental amalgam*. (An amalgam is a substance made by combining mercury with another metal or metals.) Dental amalgam actually consists of three solid phases having stoichiometries approximately corresponding to Ag_2Hg_3 , Ag_3Sn , and Sn_8Hg . The standard reduction potentials for these solid phases are: $\text{Hg}_2^{2+}||\text{Ag}_2\text{Hg}_3$, 0.85 V; $\text{Sn}^{2+}|\text{Ag}_3\text{Sn}$, -0.05 V; and $\text{Sn}^{2+}/\text{Sn}_8\text{Hg}$, -0.13 V.

Anyone who bites a piece of aluminum foil (such as that used for wrapping candies) in such a way that the foil presses against a dental filling will probably experience a momentary sharp pain. In effect, an electrochemical cell has been created in the mouth, with aluminum ($E^\circ = -1.66$ V) as the anode, the filling as the cathode, and saliva as the electrolyte. Contact between the aluminum foil and the filling short-circuits the cell, causing a weak current to flow between the electrodes. This current stimulates the sensitive nerve of the tooth, causing an unpleasant sensation.

Another type of discomfort results when a less electro-positive metal touches a dental filling. For example, if a filling makes contact with a gold inlay in a nearby tooth, corrosion of the filling will occur. In this case, the dental filling acts as the anode and the gold inlay as the cathode. Referring to the E° values for the three phases, we see that the Sn_8Hg phase is most likely to corrode. When that happens, release of $\text{Sn}(\text{II})$ ions in the mouth produces an unpleasant metallic taste. Prolonged corrosion will eventually result in another visit to the dentist for a replacement filling.



Corrosion of a dental filling brought about by contact with a gold inlay.

Continued—

where we have used the fact that, assuming ideal dilute solution behavior, the standard state for aqueous solutes is a 1 M solution. Note that to balance the overall equation we multiplied the reduction of Ag (but not E°) by 2. We can do so because, as an intensive property, E° is not affected by this procedure. We find the emf of the cell by using Equation 13.1 and Table 13.1:

$$\begin{aligned}\mathcal{E}_{\text{cell}}^\circ &= \mathcal{E}_{\text{cathode}}^\circ - \mathcal{E}_{\text{anode}}^\circ \\ &= \mathcal{E}_{\text{Ag}^+|\text{Ag}}^\circ - \mathcal{E}_{\text{Mg}^{2+}|\text{Mg}}^\circ \\ &= +0.80 \text{ V} - (-2.37 \text{ V}) \\ &= +3.17 \text{ V}\end{aligned}$$

Check The positive value of E° shows that the forward reaction is favored.

Practice Exercise What is the standard emf of a galvanic cell made of a Cd electrode in a 1.0 M $\text{Cd}(\text{NO}_3)_2$ solution and a Cr electrode in a 1.0 M $\text{Cr}(\text{NO}_3)_3$ solution at 25°C? Assume ideal dilute solution behavior.

13.4 | The Emf of an Electrochemical Cell Is Directly Related to Gibbs Free Energy Change of the Redox Reaction

In a galvanic cell, chemical energy is converted to electric energy. Electric energy in this case is the product of the emf of the cell and the total electric charge (in coulombs) that passes through the cell:

$$\begin{aligned}\text{electric energy} &= \text{volts} \times \text{coulombs} \\ &= \text{joules}\end{aligned}$$

The total charge is determined by the number of moles of electrons (n) that pass through the circuit. By definition

$$\text{total charge} = nF$$

n is the number of moles of electrons exchanged between the reducing agent and the oxidizing agent in the overall redox reaction.

where F , the **Faraday⁵ constant**, is the electric charge contained in 1 mole of electrons, which has been shown by experiment to be 96,485.3 coulombs. Thus,

$$F = 96,485.3 \text{ C mol}^{-1} e^-$$

(For most calculations it is sufficient to round F to three significant figures: $F = 96,500 \text{ C mol}^{-1}$.) Because

$$1 \text{ J} = 1 \text{ C} \times 1 \text{ V}$$

we can also express the units of the faraday constant as

$$F = 96,500 \text{ J V}^{-1} \text{ mol}^{-1}$$

The measured emf is the *maximum* voltage that the cell can achieve. This value is used to calculate the maximum amount of electric energy that can be obtained from the chemical reaction. This energy is used to do electric work (w_{ele}), so

$$\begin{aligned}w_{\text{max}} &= -w_{\text{ele}} \\ &= -nFF_{\text{cell}}\end{aligned}$$

where w_{max} is the maximum amount of work that can be done by the system. The negative sign on the right-hand side indicates that the electric work is done by the system on the surroundings.

The sign convention for electrical work is the same as that for *P-V* work, discussed in Section 7.1.

Relationship of E_{cell}° to ΔG , ΔG° , and K

In Chapter 8, we showed that the change in Gibbs free energy for a reaction ΔG represents the maximum amount of nonexpansion work that can be obtained from that reaction:

$$\Delta G = w_{\text{max}}$$

5. Michael Faraday (1791–1867). English chemist and physicist. Faraday is regarded by many as the greatest experimental scientist of the nineteenth century. He started as an apprentice to a bookbinder at the age of 13 but became interested in science after reading a book on chemistry. Faraday invented the electric motor and was the first person to demonstrate the principle governing electrical generators. Besides making notable contributions to the fields of electricity and magnetism, Faraday also worked on optical activity and discovered and named benzene.

Therefore, we can write

$$\Delta G = -nF\mathcal{E}_{\text{cell}} \quad (13.2)$$

Both n and F are positive quantities, and ΔG is negative for a spontaneous process; so $\mathcal{E}_{\text{cell}}$ must be positive for a spontaneous process.

For reactions in which reactants and products are in their standard states, Equation 13.2 becomes

$$\Delta G^\circ = -nF\mathcal{E}_{\text{cell}}^\circ \quad (13.3)$$

Now we can relate $\mathcal{E}_{\text{cell}}^\circ$ to the equilibrium constant (K) of a redox reaction. In Section 10.3, we saw that the standard free-energy change ΔG° for a reaction is related to its equilibrium constant as follows (Equation 10.12):

$$\Delta G^\circ = -RT \ln K$$

Therefore, if we combine Equations 10.12 and 13.3, we obtain

$$-nF\mathcal{E}_{\text{cell}}^\circ = -RT \ln K$$

Solving for $\mathcal{E}_{\text{cell}}^\circ$,

$$\mathcal{E}_{\text{cell}}^\circ = \frac{RT}{nF} \ln K \quad (13.4)$$

When $T = 298.15$ K, Equation 13.4 can be simplified by substituting in numerical values for R and F :

$$\mathcal{E}_{\text{cell}}^\circ = \frac{(8.3145 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{n(96485 \text{ J V}^{-1} \text{ mol}^{-1})} \ln K$$

$$\mathcal{E}_{\text{cell}}^\circ = \frac{0.025693 \text{ V}}{n} \ln K \quad (13.5)$$

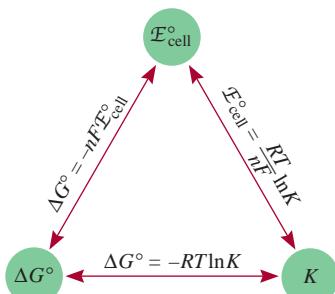


Figure 13.7 Relationships among $\mathcal{E}_{\text{cell}}^\circ$, K , and ΔG° .

Examples 13.5 and 13.6 apply Equations 13.3 through 13.5.

Table 13.2 Relationships Among ΔG° , K , and $\mathcal{E}_{\text{cell}}^\circ$

| ΔG° | K | $\mathcal{E}_{\text{cell}}^\circ$ | Reaction Under Standard-State Conditions |
|------------------|------|-----------------------------------|---|
| Negative | >1 | Positive | Favors formation of products. |
| 0 | $=1$ | 0 | Reactants and products are equally favored. |
| Positive | <1 | Negative | Favors formation of reactants. |

Example 13.5

Calculate the equilibrium constant for the following reaction at 25°C:

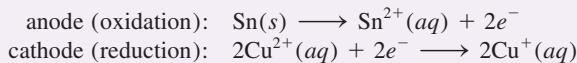


Strategy The general relationship between the equilibrium constant K and the standard emf is given by Equation 13.4; however, because the temperature is 25°C (298.15 K), we can use Equation 13.5:

$$\mathcal{E}_{\text{cell}}^{\circ} = \frac{0.025693 \text{ V}}{n} \ln K$$

Thus, if we can determine the standard emf, we can calculate the equilibrium constant. We can determine the $\mathcal{E}_{\text{cell}}^{\circ}$ of a hypothetical galvanic cell made up of two couples ($\text{Sn}^{2+}|\text{Sn}$ and $\text{Cu}^{2+}|\text{Cu}^+$) from the standard reduction potentials in Table 13.1.

Solution The half-cell reactions are



$$\begin{aligned} \mathcal{E}_{\text{cell}}^{\circ} &= \mathcal{E}_{\text{cathode}}^{\circ} - \mathcal{E}_{\text{anode}}^{\circ} \\ &= \mathcal{E}_{\text{Cu}^{2+}|\text{Cu}}^{\circ} - \mathcal{E}_{\text{Sn}^{2+}|\text{Sn}}^{\circ} \\ &= +0.15 \text{ V} - (-0.14 \text{ V}) \\ &= +0.29 \text{ V} \end{aligned}$$

Equation 13.5 can be written

$$\ln K = \frac{n\mathcal{E}_{\text{cell}}^{\circ}}{0.025693 \text{ V}}$$

In the overall reaction, two electrons are transferred, so $n = 2$. Therefore,

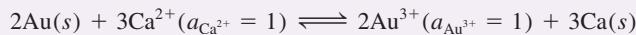
$$\begin{aligned} \ln K &= \frac{2(0.29 \text{ V})}{0.025693 \text{ V}} = 22.6 \\ K &= e^{22.6} = 7 \times 10^9 \end{aligned}$$

Check The standard emf is positive, so the reaction is spontaneous toward the products under standard conditions; therefore, K should be larger than 1.

Practice Exercise Calculate the equilibrium constant for the following reaction at 25°C:

**Example 13.6**

Calculate the standard free-energy change for the following reaction at 25°C:



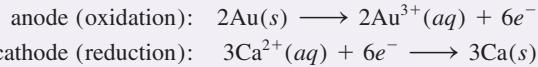
Strategy The relationship between the standard free energy change and the standard emf of the cell is given by Equation 13.3: $\Delta G^\circ = -nF\mathcal{E}_{\text{cell}}^{\circ}$. Thus, if we can determine $\mathcal{E}_{\text{cell}}^{\circ}$, we can calculate ΔG° . We can determine the $\mathcal{E}_{\text{cell}}^{\circ}$ of a hypothetical galvanic cell

—Continued

Continued—

made up of two half reactions, $\text{Au}^{3+}|\text{Au}$ and $\text{Ca}^{2+}|\text{Ca}$, from the standard reduction potentials in Table 13.1.

Solution The half-cell reactions are



$$\begin{aligned}\mathcal{E}_{\text{cell}}^{\circ} &= \mathcal{E}_{\text{cathode}}^{\circ} - \mathcal{E}_{\text{anode}}^{\circ} \\ &= \mathcal{E}_{\text{Ca}^{2+}|\text{Ca}}^{\circ} - \mathcal{E}_{\text{Au}^{3+}|\text{Au}}^{\circ} \\ &= -2.87 \text{ V} - 1.50 \text{ V} \\ &= -4.37 \text{ V}\end{aligned}$$

Now we use Equation 13.3:

$$\Delta G^{\circ} = -nF\mathcal{E}_{\text{cell}}^{\circ}$$

The overall reaction shows that $n = 6$, so

$$\begin{aligned}\Delta G^{\circ} &= -(6)(96,500 \text{ J V}^{-1} \text{ mol}^{-1})(-4.37 \text{ V}) \\ &= 2.53 \times 10^6 \text{ J mol}^{-1} \\ &= 2.53 \times 10^3 \text{ kJ mol}^{-1}\end{aligned}$$

Check The large positive value of ΔG° tells us that the reaction favors the reactants at equilibrium. The result is consistent with the fact that $\mathcal{E}_{\text{cell}}^{\circ}$ for the galvanic cell is negative.

Practice Exercise Calculate ΔG° for the following reaction at 25°C:



Temperature Dependence of Emf

As was the case for the equilibrium constant (see Section 10.4), the temperature dependence of the emf can also be determined from the thermodynamic properties of the cell. We start with the van't Hoff equation (Equation 10.16) for the temperature dependence of the equilibrium constant

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Equation 10.16 is valid as long as the temperature dependence of the enthalpy of reaction ΔH° is small. Combining Equation 13.4 [$\mathcal{E}_{\text{cell}}^{\circ} = (RT/nF)\ln K$] with Equation 10.16 gives

$$\frac{nF\mathcal{E}_{\text{cell}, T_2}^{\circ}}{RT_2} - \frac{nF\mathcal{E}_{\text{cell}, T_1}^{\circ}}{RT_1} = \frac{\Delta H^{\circ}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

which, after rearranging and dividing by F , gives

$$\frac{\mathcal{E}_{\text{cell}, T_2}^{\circ}}{T_2} = \frac{\mathcal{E}_{\text{cell}, T_1}^{\circ}}{T_1} + \frac{\Delta H^{\circ}}{nF} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (13.6)$$

Therefore, if the standard emf for a cell at a certain temperature is given, its value at another temperature can be determined using Equation 13.6 if the enthalpy change for the cell reaction is known. On the other hand, if the emf of a cell can be determined at two or more different temperatures, Equation 13.6 can be used to estimate the enthalpy change ΔH° for a cell reaction. Also, because ΔG° can be determined from one of the \mathcal{E}° measurements, the entropy change ΔS° can be determined using $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (Equation 8.35). Thus, the standard enthalpy and entropy of a reaction can be determined directly from the emf as a function of temperature, which gives us a noncalorimetric method for the calculation of these important thermodynamic quantities.

Also, we can manipulate Equation 13.6 (Problem 13.116), assuming that both ΔH° and ΔS° are independent of temperature, to give

$$\mathcal{E}_{\text{cell}, T_2}^\circ = \mathcal{E}_{\text{cell}, T_1}^\circ + \frac{\Delta S^\circ}{nF}(T_2 - T_1) \quad (13.7)$$

Thus, the change in the emf of a cell can be directly related to the standard entropy change for a cell reaction. Often the sign and magnitude of the entropy change for a reaction can be predicted qualitatively, so this gives us a way of estimating the direction and size of the temperature dependence for a reaction. For example, a cell reaction in which one of the products or reactants is a gas will generally have a larger standard entropy change than one in which all the reactants and products are in aqueous solution. Thus, we would expect the emf of the former reaction to be more affected by temperature change.

Example 13.7

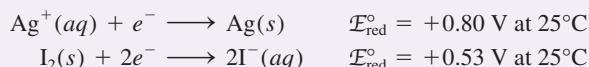
Given that the ΔH° value for the cell reaction



is $-100.0 \text{ kJ mol}^{-1}$ at 25°C , estimate the emf of this cell at 80°C . What assumptions must you make?

Strategy First find the emf of the cell at 25°C using the data in Table 13.1. For this cell, $n = 2$. To find the emf at 80°C , use Equation 13.6 and the given value of the standard enthalpy change at 25°C . Equation 13.6 assumes that ΔH° is independent of temperature over the relevant temperature range. Remember the conversion $1 \text{ V} = 1 \text{ J C}^{-1}$.

Solution From Table 13.1 the two half-reactions are



The cell emf at 25°C is then

$$\mathcal{E}_{\text{cell}}^\circ = \mathcal{E}_{\text{cathode}}^\circ - \mathcal{E}_{\text{anode}}^\circ = +0.80 \text{ V} - 0.53 \text{ V} = +0.27 \text{ V}$$

Equation 13.6 is

$$\frac{\mathcal{E}_{\text{cell}, T_2}^\circ}{T_2} = \frac{\mathcal{E}_{\text{cell}, T_1}^\circ}{T_1} + \frac{\Delta H^\circ}{nF} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

—Continued

Continued—

Substituting $T_1 = 25^\circ\text{C} = 298 \text{ K}$, $T_2 = 80^\circ\text{C} = 353 \text{ K}$, $n = 2$, and the given value of ΔH° into this equation gives

$$\frac{\mathcal{E}_{\text{cell}, T_2}^\circ}{353 \text{ K}} = \frac{0.27 \text{ V}}{298 \text{ K}} + \frac{(-100.0 \text{ kJ mol}^{-1})(1000 \text{ J kJ}^{-1})}{2(96485 \text{ C mol}^{-1})} \left(\frac{1}{298 \text{ K}} - \frac{1}{353 \text{ K}} \right)$$

$$\mathcal{E}_{\text{cell}, T_2}^\circ = 0.22 \text{ V K}^{-1}$$

Thus, the cell voltage decreases by 0.05 V when the temperature is raised from 25°C to 80°C .

Check A decrease in the cell voltage indicates a decrease in the equilibrium constant for this reaction. This reaction is exothermic. LeChâtelier's principle would predict that the equilibrium for an exothermic reaction would shift toward the reactants and decrease the equilibrium constant. Thus, our result is consistent with LeChâtelier's principle.

Practice Exercise Use the data in Table 13.1 and in Appendix 2 to determine the emf of the cell reaction

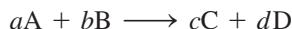


at 80°C .

13.5 | The Concentration Dependence of the Emf Can Be Determined Using the Nernst Equation

So far we have focused on redox reactions in which reactants and products are in their standard states, but there is no reason that a redox reaction of practical interest must be carried out under standard-state conditions, and, in general, the conditions will differ significantly from the standard state. Nevertheless, there is a mathematical relationship between the emf of a galvanic cell and the activities of reactants and products in a redox reaction under non-standard-state conditions.

Consider a redox reaction of the type



From Equation 10.11,

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where Q is the reaction quotient for this reaction

$$Q = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

Because $\Delta G = -nFE$ (Equation 13.2) and $\Delta G^\circ = -nFE^\circ$ (Equation 13.3), Equation 10.11 can be expressed as

$$-nFE = -nFE^\circ + RT \ln Q \quad (13.8)$$

Dividing Equation 13.8 through by $-nF$, we get

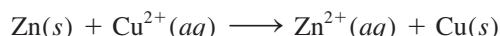
$$E = E^\circ - \frac{RT}{nF} \ln Q \quad (13.9)$$

Equation 13.9 is known as the **Nernst⁶ equation**. At 25°C (298.15 K), Equation 13.9 can be rewritten as

$$\mathcal{E}(25^\circ\text{C}) = \mathcal{E}^\circ - \frac{0.025693 \text{ V}}{n} \ln Q \quad (13.10)$$

During the operation of a galvanic cell, electrons flow from the anode to the cathode, resulting in product formation and a decrease in reactant concentration. Thus, Q increases, which means that \mathcal{E} decreases. Eventually, the cell reaches equilibrium. At equilibrium, there is no net transfer of electrons, so $\mathcal{E} = 0$, $Q = K$, where K is the equilibrium constant, and the Nernst equation (Equation 13.9) simplifies to Equation 13.4.

The Nernst equation can be used to calculate \mathcal{E} as a function of reactant and product concentrations in a redox reaction if activities can be approximated by molar concentrations. For example, for the Daniell cell in Figure 13.3,



The Nernst equation for this cell at 25°C (Equation 13.10), assuming ideal solution behavior, can be written as

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.025693 \text{ V}}{n} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

where we have used the fact that the activity of pure solids can be assumed to be unity. If the ratio $[\text{Zn}^{2+}]/[\text{Cu}^{2+}]$ is less than 1, $\ln([\text{Zn}^{2+}]/[\text{Cu}^{2+}])$ is a negative number, so that the second term on the right-hand side of the preceding equation is positive. Under this condition, \mathcal{E} is greater than the standard emf \mathcal{E}° . If the ratio is greater than 1, \mathcal{E} is smaller than \mathcal{E}° .

Example 13.8 illustrates the use of the Nernst equation.

Example 13.8

Predict whether the following reaction would proceed spontaneously as written at 298 K:



given that $[\text{Co}^{2+}] = 0.15 \text{ M}$ and $[\text{Fe}^{2+}] = 0.68 \text{ M}$. Assume ideal dilute solution behavior for the solutes.

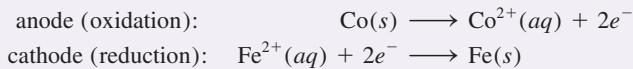
Strategy Because the reaction is not run under standard-state conditions (concentrations are not 1 M under ideal dilute solution conditions), we need to use the Nernst equation (Equation 13.10) to calculate the emf (\mathcal{E}) of a hypothetical galvanic cell and determine the spontaneity of the reaction. The standard emf (\mathcal{E}°) can be calculated using the standard reduction potentials in Table 13.1. Remember that pure solids can be considered to have an activity of 1, so they can be neglected in the Q term of the Nernst equation. Note that 2 moles of electrons are transferred per mole of reaction, that is, $n = 2$.

—Continued

6. Walter Hermann Nernst (1864–1941). German chemist and physicist. Nernst's work was mainly in electrolyte solutions and thermodynamics. He also invented an electric piano. Nernst was awarded the Nobel Prize in Chemistry in 1920 for his contribution to thermodynamics.

Continued—

Solution The half-cell reactions are



$$\begin{aligned} \mathcal{E}_{\text{cell}}^{\circ} &= \mathcal{E}_{\text{cathode}}^{\circ} - \mathcal{E}_{\text{anode}}^{\circ} \\ &= \mathcal{E}_{\text{Fe}^{2+}|\text{Fe}}^{\circ} - \mathcal{E}_{\text{Co}^{2+}|\text{Co}}^{\circ} \\ &= -0.44 \text{ V} - (-0.28 \text{ V}) \\ &= -0.16 \text{ V} \end{aligned}$$

From Equation 13.10, we write

$$\begin{aligned} \mathcal{E} &= \mathcal{E}^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q \\ &= \mathcal{E}^{\circ} - \frac{0.0257 \text{ V}}{n} \ln \frac{[\text{Co}^{2+}]}{[\text{Fe}^{2+}]} \\ &= -0.16 \text{ V} - \frac{0.025693 \text{ V}}{2} \ln \frac{0.15}{0.68} \\ &= -0.16 \text{ V} + 0.019 \text{ V} \\ &= -0.14 \text{ V} \end{aligned}$$

Because \mathcal{E} is negative, the reaction is not spontaneous in the direction written.

Practice Exercise Will the following reaction occur spontaneously at 25°C, given that $[\text{Fe}^{2+}] = 0.60 \text{ M}$ and $[\text{Cd}^{2+}] = 0.010 \text{ M}$?



Assume ideal dilute solution conditions.

Now suppose we want to determine at what ratio of $[\text{Co}^{2+}]$ to $[\text{Fe}^{2+}]$ the reaction in Example 13.7 would become spontaneous at 25°C. We can use Equation 13.10 as follows:

$$\mathcal{E} = \mathcal{E}^{\circ} - \frac{0.025693 \text{ V}}{n} \ln Q$$

We set \mathcal{E} equal to zero, which corresponds to the equilibrium situation.

$$\begin{aligned} 0 &= -0.16 \text{ V} - \frac{0.025693 \text{ V}}{2} \ln \frac{[\text{Co}^{2+}]}{[\text{Zn}^{2+}]} \\ \ln \frac{[\text{Co}^{2+}]}{[\text{Zn}^{2+}]} &= -12.5 \\ \frac{[\text{Co}^{2+}]}{[\text{Zn}^{2+}]} &= e^{-12.5} = K \end{aligned}$$

$$\text{or} \qquad K = 4 \times 10^{-6}$$

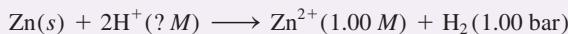
Thus, for the reaction to be spontaneous (\mathcal{E} is positive), the ratio $[\text{Co}^{2+}]/[\text{Fe}^{2+}]$ must be smaller than 4×10^{-6} .

As Example 13.9 shows, if gases are involved in the cell reaction, their concentrations should be expressed in bar.

Example 13.9

Consider the galvanic cell shown in Figure 13.6(a). In a certain experiment, the emf (\mathcal{E}) of the cell is found to be 0.54 V at 25°C. Suppose that $[Zn^{2+}] = 1.00 \times 10^{-4} M$ and $P_{H_2} = 1.00$ bar. Calculate the molar concentration of H^+ , assuming ideal solution behavior.

Strategy The equation that relates standard emf and nonstandard emf is the Nernst equation. Assuming ideal solution behavior, the standard states of Zn^{2+} and H^+ are 1 M solutions. The overall cell reaction is



Given the emf of the cell (\mathcal{E}), we apply the Nernst equation to solve for $[H^+]$. Note that 2 moles of electrons are transferred per mole of reaction, that is, $n = 2$.

Solution As we saw earlier (page 675), the standard emf (\mathcal{E}°) for the cell is 0.76 V. Because the system is at 25°C (298 K) we can use the form of the Nernst equation given in Equation 13.5:

$$\begin{aligned}\mathcal{E} &= \mathcal{E}^\circ - \frac{0.0257 \text{ V}}{n} \ln Q \\ &= \mathcal{E}^\circ - \frac{0.0257 \text{ V}}{n} \ln \frac{a_{Zn^{2+}} a_{H_2}}{a_{H^+}^2} \\ &\approx \mathcal{E}^\circ - \frac{0.0257 \text{ V}}{n} \ln \frac{[Zn^{2+}] P_{H_2}}{[H^+]^2} \\ 0.54 \text{ V} &= 0.76 \text{ V} - \frac{0.0257 \text{ V}}{2} \ln \frac{(1.00 \times 10^{-4})(1.00)}{[H^+]^2} \\ -0.34 \text{ V} &= \frac{0.0257 \text{ V}}{2} \ln \frac{1}{[H^+]^2} \\ 26.4 &= \ln \frac{1}{[H^+]^2} \\ e^{26.4} &= \frac{1}{[H^+]^2} \\ [H^+] &= \sqrt{\frac{1}{3.1 \times 10^{11}}} = 1.8 \times 10^{-6} M\end{aligned}$$

The concentrations in Q are divided by their standard-state values of 1 M; and pressures are divided by 1 bar.

Practice Exercise What is the emf of a galvanic cell consisting of a $Cd^{2+}|Cd$ half-cell and a $Pt|H^+|H_2$ half-cell if $[Cd^{2+}] = 0.20 M$, $[H^+] = 0.16 M$, and $P_{H_2} = 0.81$ bar? Assume ideal behavior.

Example 13.8 shows that a galvanic cell whose cell reaction involves H^+ ions can be used to measure the activity of H^+ or pH. In Section 10.2, we introduced the pH meter as a standard device for the measurement of pH. For the purpose of accurately and safely measuring pH in the laboratory, the hydrogen electrode itself is

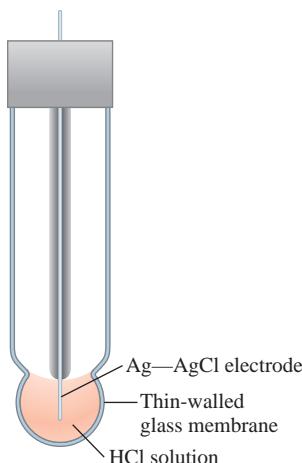


Figure 13.8 The widely used glass electrode is an example of an ion-specific electrode because it is specific to H^+ . The electrode consists of a very thin bulb or membrane made of a special type of glass that is permeable to H^+ ions. An $\text{Ag}|\text{AgCl}$ electrode is immersed in a buffer solution (constant pH) containing Cl^- ions. When the electrode is placed in a solution whose pH is different from the buffer solution, the potential difference that develops between the two sides is a measure of the difference in the two pH values.

impractical because hydrogen is explosive and the platinum electrode is susceptible to contamination, so it is replaced by a *glass electrode* (Figure 13.8). This electrode consists of a very thin glass membrane that is permeable to H^+ ions. A silver wire coated with silver chloride is immersed in a dilute hydrochloric acid solution. When the electrode is placed in a solution whose pH is different from that of the inner solutions, the potential difference that develops between the two sides of the membrane can be monitored using a reference electrode. The emf of the cell made up of the glass electrode and the reference electrode is measured with a voltmeter that is calibrated in pH units.

Concentration Cells

Because electrode potential depends on ion concentrations, it is possible to construct a galvanic cell from two half-cells composed of the *same* material but differing in ion concentrations. Such a cell is called a **concentration cell**.

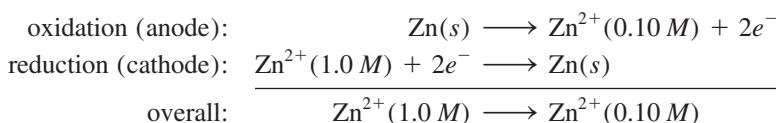
Consider a situation in which zinc electrodes are put into two aqueous solutions of zinc sulfate at 0.10 M and 1.0 M concentrations. The two solutions are connected by a salt bridge, and the electrodes are joined by a piece of wire in an arrangement like that shown in Figure 13.1. According to Le Châtelier's principle, the tendency for the reduction



increases with increasing concentration of Zn^{2+} ions. Therefore, reduction should occur in the more concentrated compartment, and oxidation should take place on the more dilute side. The cell diagram is



and the half-reactions are



The emf of the cell at 298 K (assuming ideal solution behavior), using Equation 13.5, is

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0257\text{ V}}{n} \ln \frac{[\text{Zn}^{2+}]_{\text{dil}}}{[\text{Zn}^{2+}]_{\text{conc}}}$$

where the subscripts "dil" and "conc" refer to the 0.10 M and 1.0 M concentrations, respectively. The \mathcal{E}° for this cell is zero (the same electrode and the same type of ions are involved), so

$$\begin{aligned} \mathcal{E} &= 0\text{ V} - \frac{0.0257\text{ V}}{2} \ln \frac{0.10}{1.0} \\ &= 0.0296\text{ V} \end{aligned}$$

The emf of concentration cells is usually small and decreases continually during the operation of the cell as the concentrations in the two compartments approach each other. When the concentrations of the ions in the two compartments are the same, \mathcal{E} becomes zero, and no further change occurs.

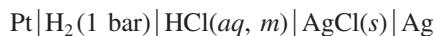
A biological cell can be compared to a concentration cell for the purpose of calculating its *membrane potential*. Membrane potential is the electrical potential that exists across the membrane of various kinds of cells, including muscle cells and nerve cells. It is responsible for the propagation of nerve impulses and heartbeat. A membrane potential is established whenever there are unequal concentrations of the same type of ion in the interior and exterior of a cell. For example, the concentrations of K⁺ ions in the interior and exterior of a nerve cell are 400 mM and 15 mM, respectively. Treating the situation as a concentration cell and applying the Nernst equation for just one kind of ions, we can write

$$\begin{aligned}\mathcal{E} &= \mathcal{E}^\circ - \frac{0.0257 \text{ V}}{1} \ln \frac{[\text{K}^+]_{\text{ex}}}{[\text{K}^+]_{\text{in}}} \\ &= -(0.0257 \text{ V}) \ln \frac{15}{400} \\ &= 0.084 \text{ V} \quad \text{or} \quad 84 \text{ mV}\end{aligned}$$

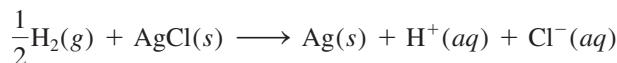
where “ex” and “in” denote exterior and interior, respectively. Note that we have set $\mathcal{E}^\circ = 0$ because the same type of ion is involved. Thus, an electrical potential of 84 mV exists across the membrane due to the unequal concentrations of K⁺ ions.

Determining Activities from Emf Measurements

Emf measurements can be used to accurately determine the activity of ions in solution. For example, consider an electrochemical cell for the reduction of silver chloride by hydrogen gas:



The overall reaction for this cell is



Using the Nernst equation appropriate to 298 K (Equation 13.10), the emf of the cell at 298 K is given by

$$\begin{aligned}\mathcal{E} &= \mathcal{E}^\circ - \frac{0.0257 \text{ V}}{n} \ln Q \\ &= \mathcal{E}^\circ - \frac{0.0257 \text{ V}}{n} \ln \frac{a_{\text{H}^+} a_{\text{Cl}^-} a_{\text{Ag}}}{a_{\text{H}_2}^{1/2} a_{\text{AgCl}}}\end{aligned}$$

Both silver (Ag) and silver chloride (AgCl) are solids so their activities are well-approximated by unity. In addition the activity of H₂ gas at 1 bar is also approximately unity. Thus, we have

$$\begin{aligned}\mathcal{E} &= \mathcal{E}^\circ - \frac{0.0257 \text{ V}}{n} \ln a_{\text{H}^+} a_{\text{Cl}^-} \\ &= \mathcal{E}^\circ - \frac{0.0257 \text{ V}}{n} \ln (\gamma_\pm m)^2\end{aligned}$$

Here $n = 1$, and we define the *mean activity coefficient*⁷ for a 1:1 electrolyte by

$$a_{\text{H}^+} a_{\text{Cl}^-} = \gamma_{\pm}^2 m^2$$

Thus, the emf of the cell is

$$\begin{aligned}\mathcal{E} &= \mathcal{E}^\circ - (0.0257 \text{ V}) \ln (\gamma_{\pm} m)^2 \\ &= \mathcal{E}^\circ - (0.0514 \text{ V}) \ln \gamma_{\pm} - (0.0514 \text{ V}) \ln m\end{aligned}$$

The preceding equation can be rearranged to give

$$\ln \gamma_{\pm} = \frac{\mathcal{E}^\circ - \mathcal{E}}{0.0514 \text{ V}} - \ln m$$

This equation can be used to determine the mean activity for a given HCl concentration from a measurement of \mathcal{E} for this cell, if the value of \mathcal{E}° is known. The value of \mathcal{E}° can be determined by measuring \mathcal{E} for this cell at very low HCl concentrations. For a very dilute solution $\gamma_{\pm} \approx 1$ and $\mathcal{E}^\circ - \mathcal{E} + (0.0514 \text{ V}) \ln m$ (See Problem 13.35).

13.6 | Batteries Use Electrochemical Reactions to Produce a Ready Supply of Electric Current

A **battery** is a galvanic cell, or a series of combined galvanic cells, that can be used as a source of direct electric current at a constant voltage. Although the operation of a battery is similar in principle to that of the galvanic cells described in Section 13.2, a battery has the advantage of being completely self-contained and requiring no auxiliary components such as salt bridges. Here we will discuss several types of batteries that are in widespread use.

The Dry Cell Battery

The most common dry cell, that is, a cell without a fluid component, is the *Leclanché cell* used in flashlights and transistor radios. The anode of the cell consists of a zinc can or container that is in contact with manganese dioxide (MnO_2) and an electrolyte. The electrolyte consists of ammonium chloride and zinc chloride in water to which starch is added to thicken the solution to a pastelike consistency so that it is less likely to leak (Figure 13.9).

A carbon rod serves as the cathode, which is immersed in the electrolyte in the center of the cell. The cell reactions are

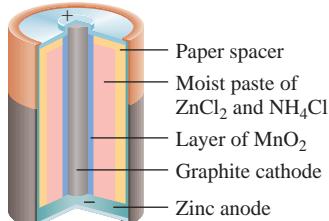
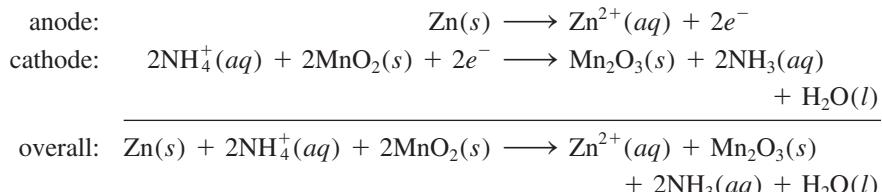


Figure 13.9 Interior section of a dry cell of the kind used in flashlights and transistor radios. Actually, the cell is not completely dry, because it contains a moist electrolyte paste.



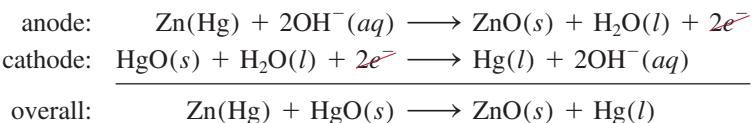
7. Because the ions Ag^+ and Cl^- cannot exist separately in solution, the individual activity coefficients of these ions are not separately defined. Instead we define a mean activity γ_{\pm} , which in this case is the geometric mean of the individual activity coefficients $\gamma_{\pm} = \sqrt{\gamma_{\text{Ag}^+} \gamma_{\text{Cl}^-}}$. For a $m:n$ electrolyte (a compound composed of cations of charge $m+$ and anions of charge n^- , for example, MgCl_2 is a 2:1 electrolyte), the mean activity coefficient is $\gamma_{\pm} = (\gamma_+^m \gamma_-^n)^{1/(m+n)}$. The mean activities for ionic compounds can be estimated using an approximation known as the Debye-Hückel theory.

Actually, this equation is an oversimplification of a complex process. The voltage produced by this dry cell is about 1.5 V, but this voltage will decrease somewhat over time because, as the reaction proceeds, the concentration $\text{NH}_4^+(aq)$ will decrease and $\text{NH}_3(aq)$ will decrease, leading to an increase in the value of Q in the Nerst equation and a decrease in the emf of the cell. The other species in the overall reaction are present in pure liquid or solid form and do not affect Q .

The Mercury Battery

The mercury battery is used extensively in medicine and the electronics industry and is more expensive than the common dry cell. Contained in a stainless-steel cylinder, the mercury battery consists of a zinc anode (amalgamated with mercury) in contact with a strongly alkaline electrolyte containing zinc oxide and mercury(II) oxide (Figure 13.10).

The cell reactions are



Because there is no change in electrolyte composition during operation—the overall cell reaction involves only solid substances—and because no aqueous species appear in the overall cell reaction, the mercury battery provides a more constant voltage (1.35 V) than the Leclanché cell. It also has a considerably higher capacity and longer life. These qualities make the mercury battery ideal for use in pacemakers, hearing aids, electric watches, and light meters.

The Lead Storage Battery

The lead storage battery commonly used in automobiles consists of six identical cells joined together in series. Each cell has a lead anode and a cathode made of lead dioxide (PbO_2) packed on a metal plate (Figure 13.11).

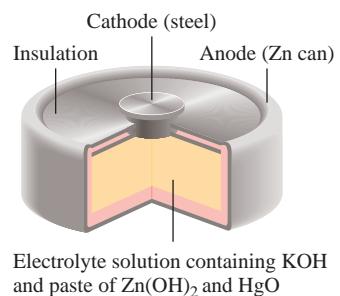


Figure 13.10 Interior section of a mercury battery.

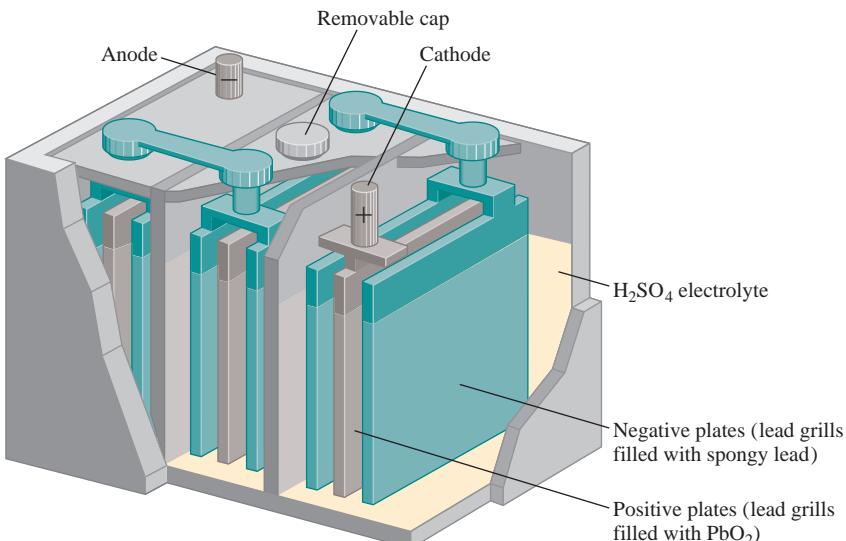
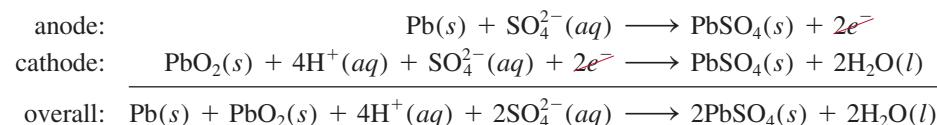


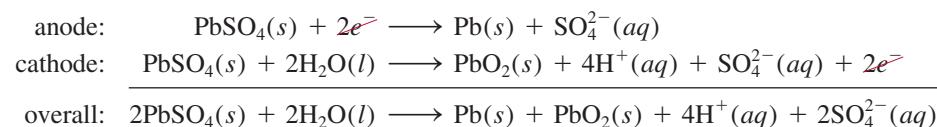
Figure 13.11 Interior section of a lead storage battery. Under normal operating conditions, the concentration of sulfuric acid solution is about 38 percent by mass.

Both the cathode and the anode are immersed in an aqueous solution of sulfuric acid, which acts as the electrolyte. The cell reactions are



Under normal operating conditions, each cell produces 2 V; a total of 12 V from the six cells is used to power the ignition circuit of the automobile and its other electric systems. The lead storage battery can deliver large amounts of current for a short time, such as the time it takes to start up the engine.

Unlike the Leclanché cell and the mercury battery, the lead storage battery is rechargeable. Recharging the battery means reversing the normal electrochemical reaction by applying an external voltage at the cathode and the anode. (This kind of process is called *electrolysis*, see Section 13.7.) The reactions that replenish the original materials are



The overall reaction is exactly the reverse of the normal cell reaction.

Two aspects of the operation of a lead storage battery are worth noting. First, because the electrochemical reaction consumes sulfuric acid, the degree to which the battery has been discharged can be checked by measuring the density of the electrolyte with a hydrometer, as is usually done at gas stations. The density of the fluid in a “healthy,” fully charged battery should be equal to or greater than 1.2 g mL^{-1} . Second, people living in cold climates sometimes have trouble starting their cars because the battery has “gone dead.” In Section 13.4, we showed that the emf of a cell is temperature dependent. However, for a lead storage battery, there is a decrease in voltage of $1.5 \times 10^{-4} \text{ V}$ for every degree Celsius drop in temperature. Thus, even allowing for a 40°C change in temperature, the decrease in voltage amounts to only $6 \times 10^{-3} \text{ V}$, which is about

$$\frac{6 \times 10^{-3} \text{ V}}{12 \text{ V}} \times 100\% = 0.05\%$$

of the operating voltage, an insignificant change. The real cause of an apparent breakdown of a battery is an increase in the viscosity of the electrolyte as the temperature decreases. For the battery to function properly, the electrolyte must be fully conducting. However, the ions move much more slowly in a viscous medium, so the resistance of the fluid increases, leading to a decrease in the power output of the battery. If an apparently “dead battery” is warmed to near room temperature on a frigid day, it recovers its ability to deliver normal power.

The Lithium-Ion Battery

Figure 13.12 shows a schematic solid-state lithium battery. The anode is made of a conducting carbonaceous material, usually graphite, which has tiny spaces in its structure that can hold both Li atoms and Li^+ ions. The cathode is made of a transition

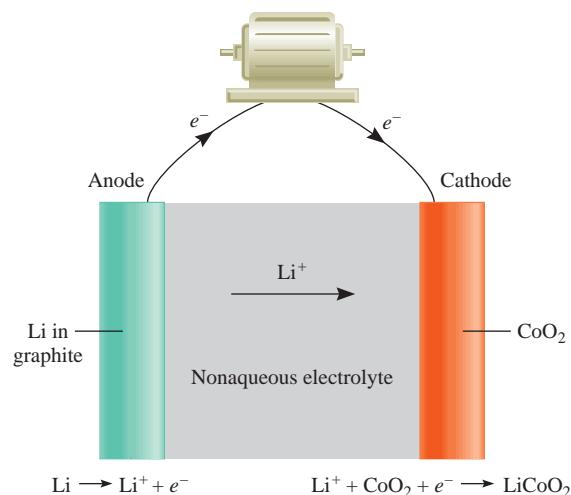
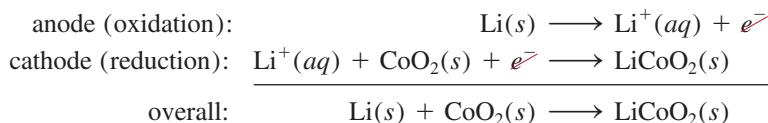


Figure 13.12 A lithium-ion type battery. Lithium atoms are embedded in the graphite, which serves as the anode and CoO_2 is the cathode. During operation, Li^+ ions migrate through the nonaqueous electrolyte from the anode to the cathode while electrons flow externally from the anode to the cathode to complete the circuit.

metal oxide such as CoO_2 , which can also hold Li^+ ions. Because of the high reactivity of the metal, a nonaqueous electrolyte (organic solvent plus dissolved salt) must be used. During the discharge of the battery, the half-cell reactions are



The advantage of the battery is that lithium has the most negative standard reduction potential value (see Table 13.1). Furthermore, lithium is the lightest metal, so that only 6.941 g of Li (its molar mass) is needed to produce 1 mole of electrons. A lithium-ion battery can be recharged literally hundreds of times without deterioration. These desirable characteristics make it suitable for use in cellular telephones, digital cameras, and laptop computers.

Fuel Cells

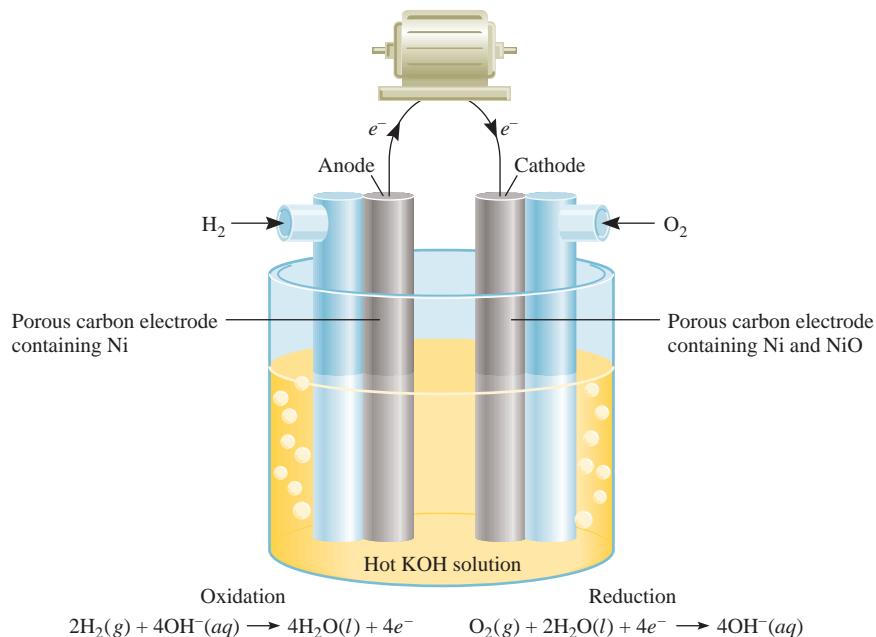
Fossil fuels are a major source of energy, but conversion of fossil fuel into electric energy is a highly inefficient process. Consider the combustion of methane:



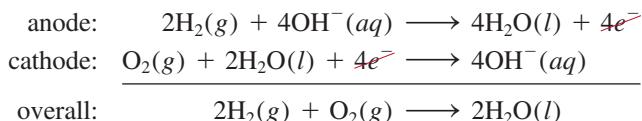
To generate electricity, heat produced by the reaction is first used to convert water to steam, which then drives a turbine that drives a generator. An appreciable fraction of the energy released in the form of heat is lost to the surroundings at each step; even the most efficient power plant converts only about 40 percent of the original chemical energy into electricity. Because combustion reactions are redox reactions, it is more desirable to carry them out directly by electrochemical means, thereby greatly increasing the efficiency of power production. This objective can be accomplished by a device known as a **fuel cell**, a galvanic cell that requires a continuous supply of reactants to keep functioning.

In its simplest form, a hydrogen-oxygen fuel cell consists of an electrolyte solution, such as potassium hydroxide solution, and two inert electrodes. Hydrogen and

Figure 13.13 A hydrogen-oxygen fuel cell. The Ni and NiO embedded in the porous carbon electrodes are electrocatalysts.



oxygen gases are bubbled through the anode and cathode compartments (Figure 13.13), where the following reactions take place:

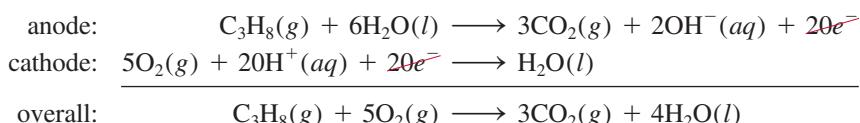


The standard emf of the cell can be calculated as follows, with data from Table 13.1:

$$\begin{aligned}\mathcal{E}_{\text{cell}}^{\circ} &= \mathcal{E}_{\text{cathode}}^{\circ} - \mathcal{E}_{\text{anode}}^{\circ} \\ &= 0.40 \text{ V} - (-0.83 \text{ V}) \\ &\equiv 1.23 \text{ V}\end{aligned}$$

Thus, the cell reaction is spontaneous under standard-state conditions. Note that the reaction is the same as the hydrogen combustion reaction, but the oxidation and reduction are carried out separately at the anode and the cathode. Like platinum in the standard hydrogen electrode, the electrodes have a two-fold function. They serve as electric conductors, and they provide the necessary surfaces for the initial decomposition of the molecules into atomic species, prior to electron transfer. They are *electrocatalysts*. Metals such as platinum, nickel, and rhodium are good electrocatalysts.

In addition to the H₂-O₂ system, a number of other fuel cells have been developed. Among these is the propane-oxygen fuel cell. The half-cell reactions are



The overall reaction is identical to the burning of propane in oxygen.

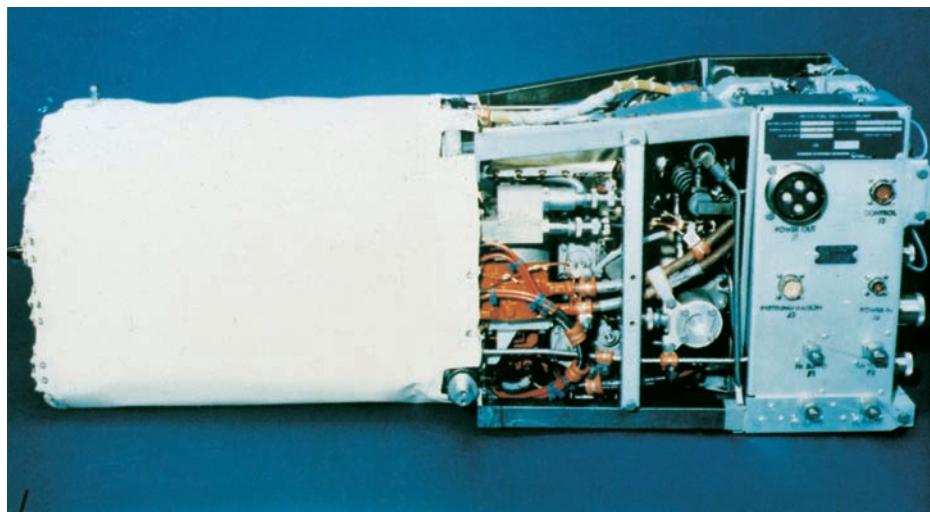


Figure 13.14 A hydrogen-oxygen fuel cell used in the space program. The pure water produced by the cell is consumed by the astronauts.

Unlike batteries, fuel cells do not store chemical energy. Reactants must be constantly resupplied, and products must be constantly removed from a fuel cell. In this respect, a fuel cell resembles an engine more than it does a battery. However, the fuel cell does not operate like a heat engine and therefore is not subject to the same kind of thermodynamic limitations in energy conversion.

Properly designed fuel cells may be as much as 70 percent efficient, about twice as efficient as an internal combustion engine. In addition, fuel-cell generators are free of the noise, vibration, heat transfer, thermal pollution, and other problems normally associated with conventional power plants. Nevertheless, fuel cells are not yet in widespread use. A major problem lies in the lack of cheap electrocatalysts able to function efficiently for long periods of time without contamination. The most successful application of fuel cells to date has been in space vehicles (Figure 13.14).

13.7 | In Electrolysis, an Electric Current Is Used to Drive a Nonspontaneous Reaction

In contrast to spontaneous redox reactions, which result in the conversion of chemical energy into electric energy, **electrolysis** is the process in which *electric energy is used to cause a nonspontaneous chemical reaction to occur*. An **electrolytic cell** is an apparatus for carrying out electrolysis. The same principles underlie electrolysis and the processes that take place in galvanic cells. Here we will discuss three examples of electrolysis based on those principles: electrolysis of molten NaCl, water, and aqueous NaCl. Then we will look at the quantitative aspects of electrolysis.

Electrolysis of Molten Sodium Chloride

In its molten state, sodium chloride, an ionic compound, can be electrolyzed to form sodium metal and chlorine. Figure 13.15(a) is a diagram of a *Downs cell*, which is used for large-scale electrolysis of NaCl. In molten NaCl, the cations and anions are the Na^+ and Cl^- ions, respectively.

Figure 13.15 (a) A Downs cell for the electrolysis of molten NaCl (m.p. 801°C). The sodium metal formed at the cathodes is in the liquid state. Because liquid sodium metal is less dense than molten NaCl, the sodium floats to the surface, as shown, and is collected. Chlorine gas forms at the anode and is collected at the top. (b) A simplified diagram showing the electrode reactions during the electrolysis of molten NaCl. The battery is needed to drive the nonspontaneous reactions.

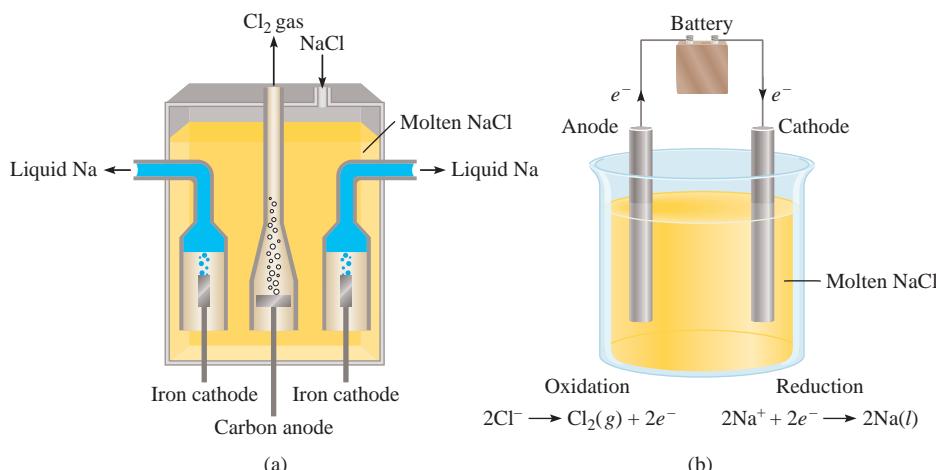
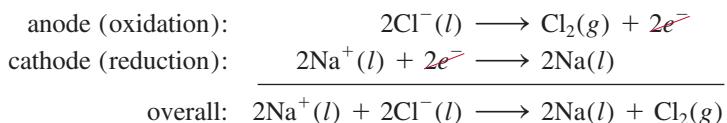


Figure 13.15(b) is a simplified diagram showing the reactions that occur at the electrodes. The electrolytic cell contains a pair of electrodes connected to the battery. The battery serves as an “electron pump,” driving electrons to the cathode, where reduction occurs, and withdrawing electrons from the anode, where oxidation occurs. The reactions at the electrodes are



This process is a major source of pure sodium metal and chlorine gas. Theoretical estimates show that the \mathcal{E}° value for the overall process is about -4 V, which means that this is a nonspontaneous process. Therefore, a *minimum* of 4 V must be supplied by the battery to carry out the reaction. In practice, a higher voltage is necessary because of inefficiencies in the electrolytic process and because of overvoltage, to be discussed shortly.

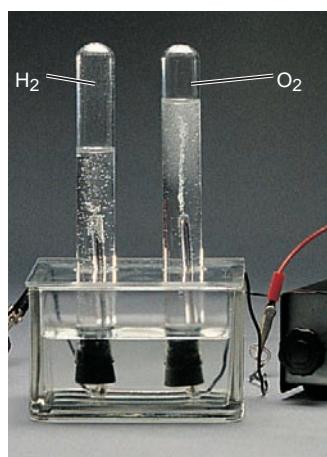
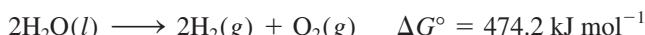


Figure 13.16 Apparatus for small-scale electrolysis of water. The volume of hydrogen gas generated is twice that of oxygen gas.

Electrolysis of Water

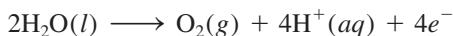
Water in a beaker under standard ambient conditions (1 bar and 25°C) will not spontaneously decompose to form hydrogen and oxygen gas because the standard free-energy change for the reaction is a large positive quantity:



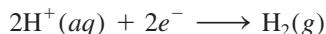
However, this reaction can be induced in a cell like the one shown in Figure 13.16.

This electrolytic cell consists of a pair of electrodes made of a nonreactive metal, such as platinum, immersed in water. When the electrodes are connected to the battery, nothing happens because there are not enough ions in pure water to carry much of an electric current. (Remember that at 25°C, pure water has only $1 \times 10^{-7} M$ H^+ ions and $1 \times 10^{-7} M$ OH^- ions.) On the other hand, the reaction occurs readily in a $0.1 M$ H_2SO_4 solution because there are a sufficient number of ions to conduct electricity. Immediately, gas bubbles begin to appear at both electrodes.

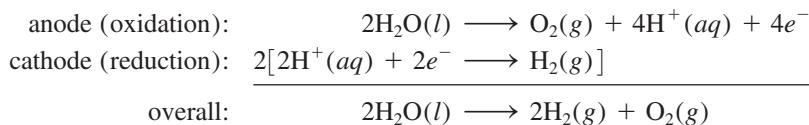
Figure 13.17 shows the electrode reactions. The process at the anode is



whereas, at the cathode we have



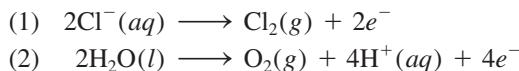
The overall reaction is given by



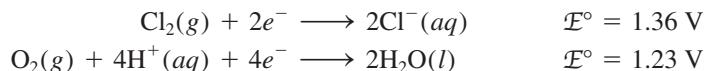
Note that no H_2SO_4 is consumed in the overall reaction.

Electrolysis of an Aqueous Sodium Chloride Solution

This is the most complicated of the three examples of electrolysis considered here because aqueous sodium chloride solution contains several species that could be oxidized and reduced. The oxidation reactions that might occur at the anode are



Referring to Table 13.1, we find



The standard reduction potentials of (1) and (2) are not very different, but the values do suggest that H_2O should be preferentially oxidized at the anode. However, by experiment we find that the gas liberated at the anode is Cl_2 , not O_2 ! In studying electrolytic processes, we sometimes find that the voltage required for a reaction is considerably higher than the electrode potential indicates. The **overvoltage** is the difference between the electrode potential and the actual voltage required to cause electrolysis. The overvoltage for O_2 formation is quite high. Therefore, under normal

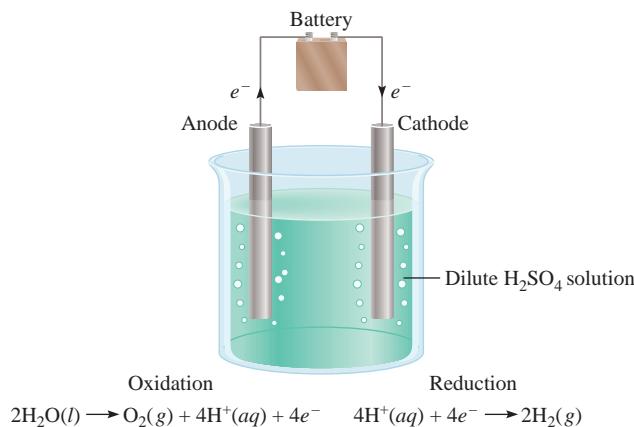
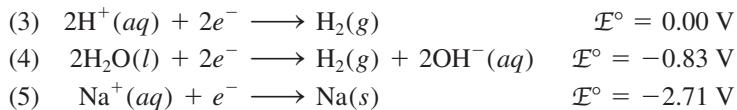
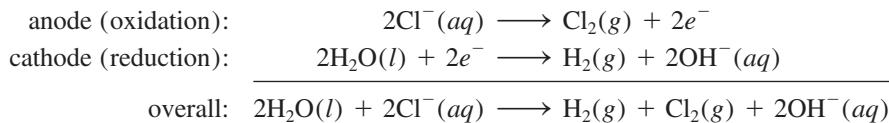


Figure 13.17 A diagram showing the electrode reactions during the electrolysis of water.

operating conditions, Cl_2 gas is actually formed at the anode instead of O_2 . The reductions that might occur at the cathode are



Reaction (5) is ruled out because it has a very negative standard reduction potential. Reaction (3) is preferred over (4) under standard-state conditions. At a pH of 7 (as is the case for an NaCl solution), however, they are equally probable. We generally use reaction (4) to describe the cathode reaction because the concentration of H^+ ions is too low (about $1 \times 10^{-7} \text{ M}$) to make reaction (3) a reasonable choice. Thus, the half-cell reactions in the electrolysis of aqueous sodium chloride are



As the overall reaction shows, the concentration of the Cl^- ions decreases during electrolysis and that of the OH^- ions increases. Therefore, in addition to H_2 and Cl_2 , the useful byproduct NaOH can be obtained by evaporating the aqueous solution at the end of the electrolysis.

Keep in mind the following from our analysis of electrolysis: cations are likely to be reduced at the cathode and anions are likely to be oxidized at the anode, and in aqueous solutions, water itself may be oxidized and/or reduced. The outcome depends on the nature of other species present.

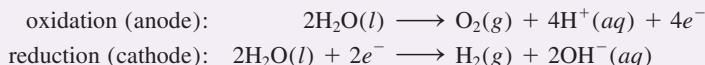
Example 13.10 deals with the electrolysis of an aqueous solution of sodium sulfate (Na_2SO_4).

Example 13.10

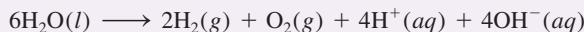
An aqueous Na_2SO_4 solution is electrolyzed, using the apparatus shown in Figure 13.16. If the products formed at the anode and cathode are oxygen gas and hydrogen gas, respectively, describe the electrolysis in terms of the reactions at the electrodes. *Note:* Na_2SO_4 does not hydrolyze.

Strategy Before we look at the electrode reactions, we should consider the following facts: (1) Because Na_2SO_4 does not hydrolyze, the pH of the solution is close to 7. (2) The Na^+ ions are not reduced at the cathode, and the SO_4^{2-} ions are not oxidized at the anode. These conclusions are drawn from the electrolysis of water in the presence of sulfuric acid and in aqueous sodium chloride solution, as discussed earlier. Therefore, both the oxidation and reduction reactions involve only water molecules.

Solution The electrode reactions are



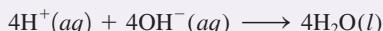
The overall reaction, obtained by doubling the cathode reaction coefficients and adding the result to the anode reaction, is



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If the H^+ and OH^- ions are allowed to mix, then



and the overall reaction becomes

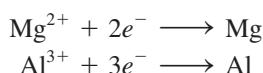


Practice Exercise An aqueous solution of $\text{Mg}(\text{NO}_3)_2$ is electrolyzed. What are the gaseous products at the anode and cathode?

Electrolysis has many important applications in industry, mainly in the extraction and purification of metals.

Quantitative Aspects of Electrolysis

The quantitative treatment of electrolysis was developed primarily by Faraday. He observed that the mass of product formed (or reactant consumed) at an electrode is proportional to both the amount of electricity transferred at the electrode and the molar mass of the substance in question. For example, in the electrolysis of molten NaCl , the cathode reaction tells us that one Na atom is produced when one Na^+ ion accepts an electron from the electrode. To reduce 1 mole of Na^+ ions, we must supply Avogadro's number (6.02×10^{23}) of electrons to the cathode. On the other hand, the stoichiometry of the anode reaction shows that oxidation of two Cl^- ions yields one chlorine molecule. Therefore, the formation of 1 mole of Cl_2 results in the transfer of 2 moles of electrons from the Cl ions to the anode. Similarly, it takes 2 moles of electrons to reduce 1 mole of Mg^{2+} ions and 3 moles of electrons to reduce 1 mole of Al^{3+} ions:



In an electrolysis experiment, we generally measure the current that passes through an electrolytic cell in a given period of time. The SI unit of current is the *ampere* (A) defined as the amount of current corresponding to 1 coulomb of charge per second.

Figure 13.18 shows the steps involved in calculating the quantities of substances produced in electrolysis. Let us illustrate the approach by considering molten CaCl_2 in an electrolytic cell. Suppose a current of 0.452 A is passed through the cell for 1.50 h. How much product will be formed at the anode and at the cathode? In solving electrolysis problems of this type, the first step is to determine which species will be oxidized at the anode and which species will be reduced at the cathode. Here the choice is straightforward because we only have Ca^{2+} and Cl^- ions in molten CaCl_2 . Thus, we write the half- and overall cell reactions as

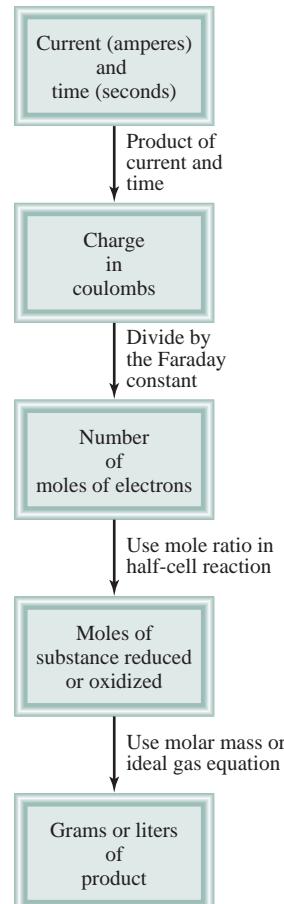
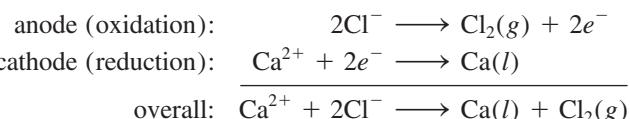


Figure 13.18 Steps involved in calculating amounts of substances reduced or oxidized in electrolysis.

The quantities of calcium metal and chlorine gas formed depend on the number of electrons that pass through the electrolytic cell, which in turn depends on current \times time, or charge:

$$\text{charge (in C)} = 0.452 \text{ A} \times 1.50 \text{ h} \times \frac{3600 \text{ s}}{\text{h}} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} = 2.44 \times 10^3 \text{ C}$$

Because 1 mol e^- = 96,500 C and 2 mol e^- are required to reduce 1 mole of Ca^{2+} ions, the mass of Ca metal formed at the cathode is calculated as follows:

$$\text{mass of Ca} = 2.44 \times 10^3 \text{ C} \times \frac{1 \text{ mol } e^-}{96,500 \text{ C}} \times \frac{1 \text{ mol Ca}}{2 \text{ mol } e^-} \times \frac{40.08 \text{ g Ca}}{1 \text{ mol Ca}} = 0.507 \text{ g Ca}$$

The anode reaction indicates that 1 mole of chlorine gas is produced per 2 mol e^- of electricity. Hence, the mass of chlorine gas formed is

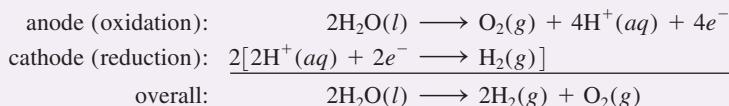
$$\text{mass of Cl}_2 = 2.44 \times 10^3 \text{ C} \times \frac{1 \text{ mol } e^-}{96,500 \text{ C}} \times \frac{1 \text{ mol Ca}}{2 \text{ mol } e^-} \times \frac{70.90 \text{ g Cl}_2}{1 \text{ mol Cl}_2} = 0.896 \text{ g Cl}_2$$

Example 13.11 applies this approach to the electrolysis in an aqueous solution.

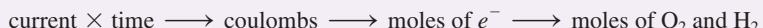
Example 13.11

A current of 1.26 A is passed through an electrolytic cell containing a dilute sulfuric acid solution for 7.44 h. Write the half-cell reactions and calculate the volume of gases generated at standard ambient temperature and pressure (SATP) (25°C and 1 bar pressure), assuming the gases behave ideally.

Strategy Earlier we saw that the half-cell reactions for the process are



According to Figure 13.18, we carry out the following conversion steps to calculate the quantity of O_2 in moles:



Then, using the ideal gas equation, we can calculate the volume of O_2 in liters at SATP. From the stoichiometry 2 moles of H_2 are produced for every mole of O_2 , so by Avogadro's law the volume of hydrogen produced should be twice that of oxygen.

Solution First we calculate the number of coulombs of electricity that pass through the cell:

$$\text{charge (in C)} = 1.26 \text{ A} \times 7.44 \text{ h} \times \frac{3600 \text{ s}}{\text{h}} \times \frac{1 \text{ C}}{1 \text{ A} \cdot \text{s}} = 3.37 \times 10^4 \text{ C}$$

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Continued—

We see that for every mole of O₂ formed at the anode, 4 moles of electrons are generated so that

$$\text{mol O}_2 = 3.37 \times 10^4 \text{ C} \times \frac{1 \text{ mol } e^-}{96,500 \text{ C}} \times \frac{1 \text{ mol Ca}}{4 \text{ mol } e^-} = 0.0873 \text{ mol O}_2$$

The volume of 0.0873 mol O₂ at SATP is given by

$$V = \frac{nRT}{P} = \frac{(0.0873 \text{ mol})(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{1 \text{ bar}} = 2.16 \text{ L}$$

The volume of H₂ produced is then 2 × 2.16 L = 4.32 L.

Check Recall from Chapter 5 that the volume of 1 mol of gas at SATP is 24.8 L. The amount of oxygen produced is slightly less than one tenth of a mole, so the volume should be slightly less than one-tenth of 24.8 = 2.48, which is true.

Practice Exercise A constant current is passed through an electrolytic cell containing molten MgCl₂ for 18 h. If 4.8 × 10⁵ g of Cl₂ are obtained, what is the current in amperes?

Summary of Facts and Concepts

Section 13.1

- ▶ Redox reactions involve the transfer of electrons. Equations representing redox processes can be balanced using the ion-electron method.
- ▶ All electrochemical reactions involve the transfer of electrons and therefore are redox reactions.

Section 13.2

- ▶ In a galvanic cell, electricity is produced by a spontaneous chemical reaction. Oxidation and reduction take place separately at the anode and cathode, respectively, and the electrons flow through an external circuit.
- ▶ The two parts of a galvanic cell are the half-cells, and the reactions at the electrodes are the half-cell reactions. A salt bridge allows ions to flow between the half-cells.

Section 13.3

- ▶ The voltage of a cell is the voltage difference between the two electrodes. In the external circuit, electrons flow from the anode to the cathode in a galvanic cell. In solution, the anions move toward the anode and the cations move toward the cathode. If the cell is operated reversibly, the cell voltage is called the electromotive force (emf).
- ▶ Standard reduction potentials show the relative likelihood of half-cell reduction reactions and can be used to

predict the products, direction, and spontaneity of redox reactions between various substances.

Section 13.4

- ▶ The emf of an electrochemical cell is directly related to the Gibbs free energy change (ΔG) of the redox reaction.
- ▶ The quantity of electricity carried by 1 mole of electrons is called the Faraday constant (F), which is equal to 96,485 C mol⁻¹.
- ▶ The temperature dependence of the emf of a cell can be determined from the thermodynamic properties of the cell reaction.

Section 13.5

- ▶ The concentration dependence of the emf can be determined using the Nernst equation.

Section 13.6

- ▶ Batteries use a spontaneous electrochemical reaction to provide a ready supply of electric current.

Section 13.7

- ▶ In electrolysis, an electric current is used to drive an electrochemical reaction in a nonspontaneous direction.

Key Words

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 battery, p. 692
 cathode, p. 673
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Problems

Oxidation-Reduction (Redox) Reactions Involve a Transfer of Electrons from One Species to Another

- 13.1 For the complete redox reactions given here, write the half-reactions and identify the oxidizing and reducing agents:
- $2\text{Sr} + \text{O}_2 \longrightarrow 2\text{SrO}$
 - $2\text{Li} + \text{H}_2 \longrightarrow 2\text{LiH}$
 - $2\text{Cs} + \text{Br}_2 \longrightarrow 2\text{CsBr}$
 - $3\text{Mg} + \text{N}_2 \longrightarrow \text{Mg}_3\text{N}_2$
- 13.2 For the complete redox reactions given here, write the half-reactions and identify the oxidizing and reducing agents:
- $4\text{Fe} + 3\text{O}_2 \longrightarrow 2\text{Fe}_2\text{O}_3$
 - $\text{Cl}_2 + 2\text{NaBr} \longrightarrow 2\text{NaCl} + \text{Br}_2$
 - $\text{Si} + 2\text{F}_2 \longrightarrow \text{SiF}_4$
 - $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$
- 13.3 Arrange the following species in order of increasing oxidation number of the sulfur atom: (a) H_2S , (b) S_8 , (c) H_2SO_4 , (d) S^{2-} , (e) HS^- , (f) SO_2 , and (g) SO_3 .
- 13.4 Phosphorus forms many oxoacids. Indicate the oxidation number of phosphorus in each of the following acids: (a) HPO_3 , (b) H_3PO_2 , (c) H_3PO_3 , (d) H_3PO_4 , (e) $\text{H}_4\text{P}_2\text{O}_7$, and (f) $\text{H}_5\text{P}_3\text{O}_{10}$.
- 13.5 Give oxidation numbers for all atoms in the following molecules and ions: (a) ClF , (b) IF_7 , (c) CH_4 , (d) C_2H_2 , (e) C_2H_4 , (f) K_2CrO_4 , (g) $\text{K}_2\text{Cr}_2\text{O}_7$, (h) KMnO_4 , (i) NaHCO_3 , (j) Li_2 , (k) NaIO_3 , (l) KO_2 , (m) PF_6^- , and (n) KAuCl_4 .
- 13.6 Give oxidation numbers for all atoms in the following molecules and ions: (a) Cs_2O , (b) CaI_2 , (c) Al_2O_3 , (d) H_3AsO_3 , (e) TiO_2 , (f) MoO_4^{2-} , (g) PtCl_4^{2-} , (h) PtCl_6^{2-} , (i) SnF_2 , (j) ClF_3 , and (k) SbF_6^- .
- 13.7 Give oxidation numbers for all atoms in the following molecules and ions: (a) Mg_3N_2 , (b) CsO_2 , (c) CaC_2 , (d) CO_3^{2-} , (e) $\text{C}_2\text{O}_4^{2-}$, (f) ZnO_2^{2-} , (g) NaBH_4 , and (h) WO_4^{2-} .
- 13.8 Nitric acid is a strong oxidizing agent. State which of the following species is *least* likely to be produced

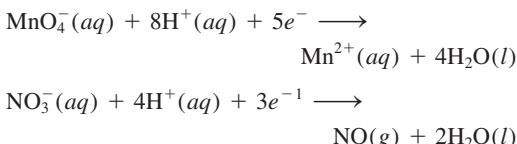
when nitric acid reacts with a strong reducing agent such as zinc metal, and explain why: N_2O , NO , NO_2 , N_2O_4 , N_2O_5 , and NH_4^+ .

- 13.9 On the basis of oxidation number considerations, one of the following oxides would not react with molecular oxygen: NO , N_2O , SO_2 , SO_3 , and P_4O_6 . Which one is it? Why?
- 13.10 Balance the following redox equations by the ion-electron method:
- $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{H}_2\text{O}$ (in acidic solution)
 - $\text{Cu}^+ + \text{HNO}_3 \longrightarrow \text{Cu}^{2+} + \text{NO} + \text{H}_2\text{O}$ (in acidic solution)
 - $\text{CN}^- + \text{MnO} \longrightarrow \text{CNO}^- + \text{MnO}_2$ (in basic solution)
 - $\text{Br}_2 \longrightarrow \text{BrO}_3^- + \text{Br}^-$ (in basic solution)
 - $\text{S}_2\text{O}_3^{2-} + \text{I}_2 \longrightarrow \text{I}^- + \text{S}_4\text{O}_6^{2-}$ (in acidic solution)
- 13.11 Balance the following redox equations by the ion-electron method:
- $\text{Mn}^{2+} + \text{H}_2\text{O}_2 \longrightarrow \text{MnO}_2 + \text{H}_2\text{O}$ (in basic solution)
 - $\text{Bi}(\text{OH})_3 + \text{SnO}_2^{2-} \longrightarrow \text{SnO}_3^{2-} + \text{Bi}$ (in basic solution)
 - $\text{Cr}_2\text{O}_7^{2-} + \text{C}_2\text{O}_4^{2-} \longrightarrow \text{Cr}^{3+} + \text{CO}_2$ (in acidic solution)
 - $\text{ClO}_3^- + \text{Cl}^- \longrightarrow \text{Cl}_2 + \text{ClO}_2^-$ (in acidic solution)

The Standard Emf of Any Electrochemical Cell Can Be Determined If the Standard Reduction Potentials for the Half-Reactions Are Known

- 13.12 Calculate the standard emf for the reactions implied by the following cell diagrams at 298 K. For each, write the overall reaction and identify which electrode would be the cathode under standard-state conditions.
- $\text{Fe}(s)|\text{Fe}^{2+}(aq)||\text{Cr}^{3+}(aq)|\text{Cr}(s)$
 - $\text{Zn}(s)|\text{Zn}^{2+}(aq)||\text{Al}^{3+}(aq)|\text{Al}(s)$
 - $\text{Mg}(s)|\text{Mg}^{2+}(aq)||\text{Pb}^{2+}(aq)|\text{Pb}(s)$

- 13.13 Calculate the standard emf of a cell that uses $\text{Ag}|\text{Ag}^+$ and $\text{Al}|\text{Al}^{3+}$ half-cell reactions. Write the overall cell reaction that occurs under standard-state conditions.
- 13.14 Predict whether Fe^{3+} can oxidize I^- to I_2 under standard-state conditions.
- 13.15 Which of the following reagents can oxidize H_2O to $\text{O}_2(g)$ under standard-state conditions: (a) $\text{H}^+(aq)$, (b) $\text{Cl}^-(aq)$, (c) $\text{Cl}_2(g)$, (d) $\text{Cu}^{2+}(aq)$, (e) $\text{Pb}^{2+}(aq)$, or (f) $\text{MnO}_4^-(aq)$ (in acid)?
- 13.16 Consider the following half-reactions:



Predict whether NO_3^- ions will oxidize Mn^{2+} to MnO_4^- under standard-state conditions.

- 13.17 Predict whether the following reactions would occur spontaneously in aqueous solution at 25°C. Assume all species are in their standard states.
- (a) $\text{Ca}(s) + \text{Cd}^{2+}(aq) \longrightarrow \text{Ca}^{2+}(aq) + \text{Cd}(s)$
 (b) $2\text{Br}(aq) + \text{Sn}^{2+}(aq) \longrightarrow \text{Br}_2(l) + \text{Sn}(s)$
 (c) $2\text{Ag}(s) + \text{Ni}^{2+}(aq) \longrightarrow 2\text{Ag}^+(aq) + \text{Ni}(s)$
 (d) $\text{Cu}(aq) + \text{Fe}^{3+}(aq) \longrightarrow \text{Cu}^{2+}(aq) + \text{Fe}^{2+}(aq)$
- 13.18 Which species in each pair is a better reducing agent under standard-state conditions: (a) Na or Li, (b) H_2 or I_2 , (c) Fe^{2+} or Ag, or (d) Br^- or Co^{2+} ?

The Emf of an Electrochemical Cell Is Directly Related to the Gibbs Free-Energy Change of the Redox Reaction

- 13.19 What is the equilibrium constant for the following reaction at 25°C?

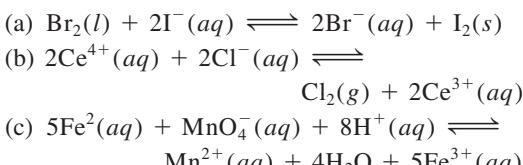


- 13.20 The equilibrium constant for the reaction

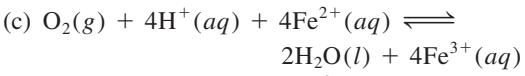
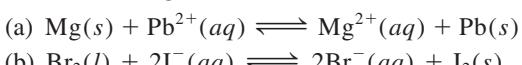


is 2.69×10^{12} at 25°C. Calculate \mathcal{E}° for a cell made up of $\text{Sr}|\text{Sr}^{2+}$ and $\text{Mg}|\text{Mg}^{2+}$ half-cells.

- 13.21 Use the standard reduction potentials to find the equilibrium constant for each of the following reactions at 25°C:



- 13.22 Using data from Table 13.1, calculate ΔG° and K_c for the following reactions at 25°C:



- 13.23 Under standard-state conditions, what spontaneous reaction will occur in aqueous solution among the ions Ce^{4+} , Ce^{3+} , Fe^{3+} , and Fe^{2+} ? Calculate ΔG° and K_c for the reaction.
- 13.24 Given that $\mathcal{E}^\circ = 0.52$ V for the reduction $\text{Cu}^+(aq) + e^- \longrightarrow \text{Cu}(s)$, calculate \mathcal{E}° , ΔG° , and K for the following reaction at 25°C:



- 13.25 Calculate the emf of the cell reaction



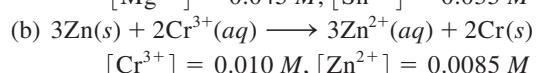
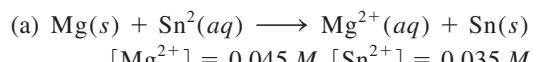
at 70°C. Explain any assumptions that you make.

- 13.26 For a certain redox reaction with $\Delta n = 1$, it is determined that the standard emf increases by 0.124 V if the temperature is changed from 25°C to 50°C. From this information, estimate the standard entropy change for this reaction. Explain any assumptions that you make.

The Concentration Dependence of the Emf Can Be Determined Using the Nernst Equation

- 13.27 What is the potential of a cell made up of $\text{Zn}|\text{Zn}^{2+}$ and $\text{Cu}|\text{Cu}^{2+}$ half-cells at 25°C if $[\text{Zn}^{2+}] = 0.25$ M and $[\text{Cu}^{2+}] = 0.15$ M? Assume ideal behavior.

- 13.28 Calculate \mathcal{E}° , \mathcal{E} , and ΔG for the following cell reactions. Assume ideal behavior.



- 13.29 Calculate the standard potential of the cell consisting of the $\text{Zn}|\text{Zn}^{2+}$ half-cell and the standard hydrogen electrode. What will be the emf of the cell if $[\text{Zn}^2] = 0.45$ M, $P_{\text{H}_2} = 2.0$ bar, and $[\text{H}^+] = 1.8$ M? Discuss any assumptions that you make.

- 13.30 What is the emf of a cell consisting of a $\text{Pb}^2|\text{Pb}$ half-cell and a $\text{Pt}|\text{H}^+|\text{H}_2$ half-cell if $[\text{Pb}^{2+}] = 0.10$ M, $[\text{H}^+] = 0.050$ M, and $P_{\text{H}_2} = 1.0$ bar? Discuss any assumptions that you make.

- 13.31 Consider a Daniell cell operating under non-standard-state conditions. Suppose that the cell reaction is multiplied by 2. What effect does this have on each of the following quantities in the Nernst equation: (a) \mathcal{E}° , (b) \mathcal{E} , (c) Q , (d) $\ln Q$, and (e) n ?

- 13.32 Referring to the arrangement in Figure 13.1, calculate the $[\text{Cu}^{2+}]/[\text{Zn}^{2+}]$ ratio at which the following reaction is spontaneous at 25°C:



- 13.33 Calculate the emf of the following concentration cell (assuming ideal behavior):



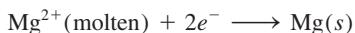
- 13.34 Consider a concentration cell consisting of two hydrogen electrodes (Figure 13.5). At 25°C, the cell emf is found to be 0.0121 V. If the pressure of the gas at the anode is 2.5 bar, what is the pressure of hydrogen gas at the cathode?
- 13.35 Calculate the emf of the Daniell cell at 25°C when the concentrations of CuSO₄ and ZnSO₄ are 0.50 M and 0.10 M respectively. What would be the emf if activities were used instead of concentrations? (The γ^\pm for CuSO₄ and ZnSO₄ at their respective concentrations are 0.068 and 0.15, respectively.)

Batteries Use Electrochemical Reactions to Produce a Ready Supply of Electric Current

- 13.36 The hydrogen-oxygen fuel cell is described in Section 13.6. (a) What volume of H₂(g), stored at 25°C at a pressure of 155 bar, would be needed to run an electric motor drawing a current of 8.5 A for 3.0 h? (b) What volume (liters) of air at 25°C and 1.00 bar will have to pass into the cell per minute to run the motor? Assume that air is 20 percent O₂ by volume and that all the O₂ is consumed in the cell. The other components of air do not affect the fuel-cell reactions. Assume ideal gas behavior.
- 13.37 Calculate the standard emf of the propane fuel cell discussed on page 696 at 25°C, given that ΔG_f° for propane is $-23.5 \text{ kJ mol}^{-1}$.

In Electrolysis, an Electric Current Is Used to Drive a Nonspontaneous Reaction

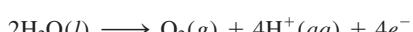
- 13.38 The half-reaction at an electrode is



Calculate the number of grams of magnesium that can be produced by supplying 1.00 F to the electrode.

- 13.39 Consider the electrolysis of molten barium chloride (BaCl₂). (a) Write the half-reactions. (b) How many grams of barium metal can be produced by supplying 0.50 A for 30 min?
- 13.40 Considering only the cost of electricity, would it be cheaper to produce a ton of sodium or a ton of aluminum by electrolysis?

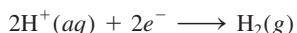
- 13.41 If the cost of electricity to produce magnesium by the electrolysis of molten magnesium chloride is \$155 per ton of metal, what is the cost (in dollars) of the electricity necessary to produce (a) 10.0 tons of aluminum, (b) 30.0 tons of sodium, (c) 50.0 tons of calcium?
- 13.42 One of the half-reactions for the electrolysis of water is



If 0.076 L of O₂ is collected at 25°C and 755 mmHg, how many moles of electrons had to pass through the solution?

- 13.43 How many faradays of electricity are required to produce (a) 0.84 L of O₂ at exactly 1 bar and 25°C from aqueous H₂SO₄ solution; (b) 1.50 L of Cl₂ at 750 mmHg and 20°C from molten NaCl; and (c) 6.0 g of Sn from molten SnCl₂?
- 13.44 Calculate the amounts of Cu and Br₂ produced in 1.0 h at inert electrodes in a solution of CuBr₂ by a current of 4.50 A.
- 13.45 In the electrolysis of an aqueous AgNO₃ solution, 0.67 g of Ag is deposited after a certain period of time. (a) Write the half-reaction for the reduction of Ag⁺. (b) What is the probable oxidation half-reaction? (c) Calculate the quantity of electricity used, in coulombs.
- 13.46 A steady current was passed through molten CoSO₄ until 2.35 g of metallic cobalt was produced. Calculate the number of coulombs of electricity used.
- 13.47 A constant electric current flows for 3.75 h through two electrolytic cells connected in series. One contains a solution of AgNO₃ and the second a solution of CuCl₂. During this time, 2.00 g of silver is deposited in the first cell. (a) How many grams of copper are deposited in the second cell? (b) What is the current flowing, in amperes?
- 13.48 What is the hourly production rate of chlorine gas (in kg) from an electrolytic cell using aqueous NaCl electrolyte and carrying a current of 1.500×10^3 A? The anode efficiency for the oxidation of Cl⁻ is 93.0 percent.
- 13.49 Chromium plating is applied by electrolysis to objects suspended in a dichromate solution, according to the following (unbalanced) half-reaction:
- $$\text{Cr}_2\text{O}_7^{2-}(aq) + e^- + \text{H}^+(aq) \longrightarrow \text{Cr}(s) + \text{H}_2\text{O}(l)$$
- How long (in hours) would it take to apply a chromium plating 1.0×10^{-2} mm thick to a car bumper with a surface area of 0.25 m² in an electrolytic cell carrying a current of 25.0 A? (The density of chromium is 7.19 g cm⁻³.)
- 13.50 The passage of a current of 0.750 A for 25.0 min deposited 0.369 g of copper from a CuSO₄ solution. From this information, calculate the molar mass of copper.
- 13.51 A quantity of 0.300 g of copper was deposited from a CuSO₄ solution by passing a current of 3.00 A through the solution for 304 s. Calculate the value of the faraday constant.
- 13.52 In a certain electrolysis experiment, 1.44 g of Ag was deposited in one cell (containing an aqueous AgNO₃ solution), while 0.120 g of an unknown metal X was deposited in another cell (containing an aqueous XCl₃ solution) in series with the AgNO₃ cell. Calculate the molar mass of X.

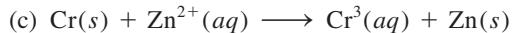
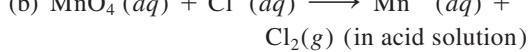
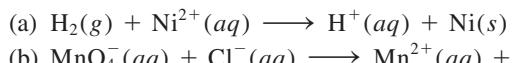
- 13.53 One of the half-reactions for the electrolysis of water is



If 0.845 L of H_2 is collected at 25°C and 782 mmHg, how many moles of electrons had to pass through the solution?

Additional Problems

- 13.54 For each of the following redox reactions, (i) write the half-reactions, (ii) write a balanced equation for the whole reaction, and (iii) determine in which direction the reaction will proceed spontaneously under standard-state conditions:



- 13.55 The oxidation of 25.0 mL of a solution containing Fe^{2+} requires 26.0 mL of 0.0250 M $\text{K}_2\text{Cr}_2\text{O}_7$ in acidic solution. Balance the following equation and calculate the molar concentration of Fe^{2+} :



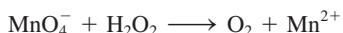
- 13.56 The SO_2 present in air is mainly responsible for the phenomenon of acid rain. The concentration of SO_2 can be determined by titrating against a standard permanganate solution as follows:



Calculate the number of grams of SO_2 in a sample of air if 7.37 mL of 0.00800 M KMnO_4 solution is required for the titration.

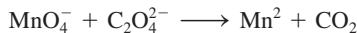
- 13.57 A sample of iron ore weighing 0.2792 g was dissolved in an excess of a dilute acid solution. All the iron was first converted to $\text{Fe}(\text{II})$ ions. The solution then required 23.30 mL of 0.0194 M KMnO_4 for oxidation to $\text{Fe}(\text{III})$ ions. Calculate the percent by mass of iron in the ore.

- 13.58 The concentration of a hydrogen peroxide solution can be conveniently determined by titration against a standardized potassium permanganate solution in an acidic medium according to the following unbalanced equation:



- (a) Balance this equation. (b) If 36.44 mL of a 0.01652 M KMnO_4 solution is required to completely oxidize 25.00 mL of an H_2O_2 solution, calculate the molarity of the H_2O_2 solution.

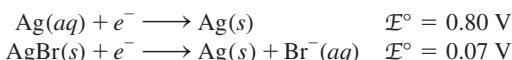
- 13.59 Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) is present in many plants and vegetables. (a) Balance the following equation in acid solution:



- (b) If a 1.00-g sample of $\text{H}_2\text{C}_2\text{O}_4$ requires 24.0 mL of 0.0100 M KMnO_4 solution to reach the equivalence point, what is the percent by mass of $\text{H}_2\text{C}_2\text{O}_4$ in the sample?

- 13.60 Calcium oxalate (CaC_2O_4) is insoluble in water. This property has been used to determine the amount of Ca^{2+} ions in blood. The calcium oxalate isolated from blood is dissolved in acid and titrated against a standardized KMnO_4 solution as described in Problem 13.59. In one test, it is found that the calcium oxalate isolated from a 10.0-mL sample of blood requires 24.2 mL of 9.56×10^{-4} M KMnO_4 for titration. Calculate the number of milligrams of calcium per milliliter of blood.

- 13.61 From the following information, calculate the solubility product of AgBr :

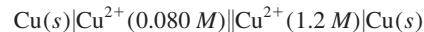


- 13.62 Consider a galvanic cell composed of the standard hydrogen electrode and a half-cell using the reaction $\text{Ag}(\text{aq}) + e^- \longrightarrow \text{Ag}(\text{s})$. (a) Calculate the standard cell potential. (b) What is the spontaneous cell reaction under standard-state conditions? (c) Calculate the cell potential when $[\text{H}^+]$ in the hydrogen electrode is changed to (i) 1.0×10^{-2} M and (ii) 1.0×10^{-5} M, all other reagents being held at standard-state conditions. (d) Based on this cell arrangement, suggest a design for a pH meter.

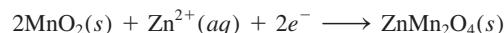
- 13.63 A galvanic cell consists of a silver electrode in contact with 346 mL of 0.100 M AgNO_3 solution and a magnesium electrode in contact with 288 mL of 0.100 M $\text{Mg}(\text{NO}_3)_2$ solution. (a) Calculate \mathcal{E} for the cell at 25°C. (b) A current is drawn from the cell until 1.20 g of silver have been deposited at the silver electrode. Calculate \mathcal{E} for the cell at this stage of operation.

- 13.64 Explain why chlorine gas can be prepared by electrolyzing an aqueous solution of NaCl but fluorine gas cannot be prepared by electrolyzing an aqueous solution of NaF .

- 13.65 Assuming ideal behavior, calculate the emf of the following concentration cell at 25°C:



- 13.66 The cathode reaction in the Leclanché cell is given by



If a Leclanché cell produces a current of 0.0050 A, calculate how many hours this current supply will last if there are initially 4.0 g of MnO_2 present in the cell. Assume that there is an excess of Zn^{2+} ions.

- 13.67 For a number of years, it was not clear whether mercury(I) ions existed in solution as Hg^+ or as

Hg_2^{2+} . To distinguish between these two possibilities, we could set up the following system:



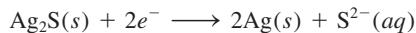
where soln A contained 0.263 g mercury(I) nitrate per liter and soln B contained 2.63 g mercury(I) nitrate per liter. If the measured emf of such a cell is 0.0289 V at 18°C, what can you deduce about the nature of the mercury(I) ions?

- 13.68 An aqueous KI solution to which a few drops of phenolphthalein have been added is electrolyzed using an apparatus like the one shown here:



Describe what you would observe at the anode and the cathode. (*Hint:* Molecular iodine is only slightly soluble in water, but in the presence of I^- ions, it forms the brown color of I_3^- ions.)

- 13.69 A piece of magnesium metal with a mass of 1.56 g is placed in 100.0 mL of 0.100 M AgNO_3 at 25°C. Calculate $[\text{Mg}^{2+}]$ and $[\text{Ag}^+]$ in solution at equilibrium. What is the mass of the leftover magnesium? The volume remains constant.
- 13.70 Steel hardware, including nuts and bolts, is often coated with a thin plating of cadmium. Explain the function of the cadmium layer.
- 13.71 “Galvanized iron” is steel sheet that has been coated with zinc; “tin” cans are made of steel sheet coated with tin. Discuss the functions of these coatings and the electrochemistry of the corrosion reactions that occur if an electrolyte contacts the scratched surface of a galvanized iron sheet or a tin can.
- 13.72 Tarnished silver contains Ag_2S . The tarnish can be removed by placing silverware in an aluminum pan containing an inert electrolyte solution, such as NaCl. Explain the electrochemical principle for this procedure. [The standard reduction potential for the half-cell reaction

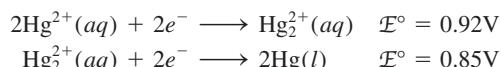


is 0.71 V.]

- 13.73 How does the tendency of iron to rust depend on the pH of the solution?
- 13.74 An acidified solution was electrolyzed using copper electrodes. A constant current of 1.18 A caused the

anode to lose 0.584 g after 1.52×10^3 s. (a) What is the gas produced at the cathode, and what is its volume at SATP? (b) Given that the charge of an electron is 1.6022×10^{-19} C, calculate Avogadro’s number. Assume that copper is oxidized to Cu^{2+} ions.

- 13.75 In a certain electrolysis experiment involving Al^{3+} ions, 60.2 g of Al is recovered when a current of 0.352 A is used. How many minutes did the electrolysis last?
- 13.76 Consider the oxidation of ammonia:
- $$4\text{NH}_3(g) + 3\text{O}_2(g) \longrightarrow 2\text{N}_2(g) + 6\text{H}_2\text{O}(l)$$
- (a) Calculate the ΔG° for the reaction. (b) If this reaction were used in a fuel cell, what would be the standard cell potential?
- 13.77 When an aqueous solution containing gold(III) salt is electrolyzed, metallic gold is deposited at the cathode and oxygen gas is generated at the anode. (a) If 9.26 g of Au is deposited at the cathode, calculate the volume (in liters) of O_2 generated at 23°C and 747 mmHg. (b) What is the current used if the electrolytic process took 2.00 h?
- 13.78 A galvanic cell is constructed by immersing a piece of copper wire in 25.0 mL of a 0.20 M CuSO_4 solution and a zinc strip in 25.0 mL of a 0.20 M ZnSO_4 solution. (a) Calculate the emf of the cell at 25°C and predict what would happen if a small amount of concentrated NH_3 solution were added to (i) the CuSO_4 solution and (ii) the ZnSO_4 solution. Assume that the volume in each compartment remains constant at 25.0 mL. (b) In a separate experiment, 25.0 mL of 3.00 M NH_3 is added to the CuSO_4 solution. If the emf of the cell is 0.68 V calculate the formation constant (K_f) of $\text{Cu}(\text{NH}_3)_4^{2+}$.
- 13.79 In an electrolysis experiment, a student passes the same quantity of electricity through two electrolytic cells, one containing a silver salt and the other a gold salt. Over a certain period of time, she finds that 2.64 g of Ag and 1.61 g of Au are deposited at the cathodes. What is the oxidation state of gold in the gold salt?
- 13.80 People living in cold-climate countries where there is plenty of snow are advised not to heat their garages in the winter. What is the electrochemical basis for this recommendation?
- 13.81 Given that



calculate ΔG° and K for the following process at 25°C:

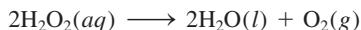


- (The preceding reaction is an example of a *disproportionation reaction* in which an element in one oxidation state is both oxidized and reduced.)
- 13.82 Fluorine (F_2) is obtained by the electrolysis of liquid hydrogen fluoride (HF) containing potassium fluoride (KF). (a) Write the half-cell reactions and the overall reaction for the process. (b) What is the purpose of KF? (c) Calculate the volume of F_2 (in liters) collected at 24.0°C and 1.2 bar after electrolyzing the solution for 15 h at a current of 502 A.
- 13.83 A 300-mL solution of NaCl was electrolyzed for 6.00 min. If the pH of the final solution was 12.24, calculate the average current used.
- 13.84 Industrially, copper is purified by electrolysis. The impure copper acts as the anode, and the cathode is made of pure copper. The electrodes are immersed in a CuSO_4 solution. During electrolysis, copper at the anode enters the solution as Cu^{2+} while Cu^{2+} ions are reduced at the cathode. (a) Write half-cell reactions and the overall reaction for the electrolytic process. (b) Suppose the anode was contaminated with Zn and Ag. Explain what happens to these impurities during electrolysis. (c) How many hours will it take to obtain 1.00 kg of Cu at a current of 18.9 A?
- 13.85 An aqueous solution of a platinum salt is electrolyzed at a current of 2.50 A for 2.00 h. As a result, 9.09 g of metallic Pt is formed at the cathode. Calculate the charge on the Pt ions in this solution.
- 13.86 Consider a galvanic cell consisting of a magnesium electrode in contact with $1.0 \text{ M } \text{Mg}(\text{NO}_3)_2$ and a cadmium electrode in contact with $1.0 \text{ M } \text{Cd}(\text{NO}_3)_2$. Calculate E° for the cell, and draw a diagram showing the cathode, anode, and direction of electron flow.
- 13.87 A current of 6.00 A passes through an electrolytic cell containing dilute sulfuric acid for 3.40 h. If the volume of O_2 gas generated at the anode is 4.26 L (at 0°C and 1 bar pressure), calculate the charge (in coulombs) on an electron.
- 13.88 Gold will not dissolve in either concentrated nitric acid or concentrated hydrochloric acid. However, the metal does dissolve in a mixture of the acids (one part HNO_3 and three parts HCl by volume), called *aqua regia*. (a) Write a balanced equation for this reaction. (Hint: Among the products are HAuCl_4 and NO_2). (b) What is the function of HCl?
- 13.89 Explain why most useful galvanic cells give voltages of no more than 1.5 to 2.5 V. What are the prospects for developing practical galvanic cells with voltages of 5 V or more?
- 13.90 A silver rod and a SHE are dipped into a saturated aqueous solution of silver oxalate ($\text{Ag}_2\text{C}_2\text{O}_4$) at 25°C . The measured potential difference between the rod and the SHE is 0.589 V, the rod being positive. Calculate the solubility product constant for silver oxalate.
- 13.91 Zinc is an amphoteric metal, that is, it reacts with both acids and bases. The standard reduction potential is -1.36 V for the reaction
- $$\text{Zn}(\text{OH})_4^{2-}(\text{aq}) + 2e^- \longrightarrow \text{Zn}(s) + 4\text{OH}^-(\text{aq})$$
- Calculate the formation constant (K_f) for the reaction
- $$\text{Zn}^{2+}(\text{aq}) + 4\text{OH}^-(\text{aq}) \rightleftharpoons \text{Zn}(\text{OH})_4^{2-}(\text{aq})$$
- 13.92 Use the data in Table 13.1 to determine whether or not hydrogen peroxide will undergo disproportionation in an acid medium:
- $$2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$$
- 13.93 The magnitudes (but *not* the signs) of the standard reduction potentials of two metals X and Y are
- $$\begin{array}{ll} \text{Y}^{2+} + 2e^- \longrightarrow \text{Y} & |E^\circ| = 0.34 \text{ V} \\ \text{X}^{2+} + 2e^- \longrightarrow \text{X} & |E^\circ| = 0.25 \text{ V} \end{array}$$
- where the notation || denotes that only the magnitude (but not the sign) of the E° value is shown. When the half-cells of X and Y are connected, electrons flow from X to Y. When X is connected to a SHE, electrons flow from X to the SHE. (a) Are the E° values of the half-reactions positive or negative? (b) What is the standard emf of a cell made up of X and Y?
- 13.94 A galvanic cell is constructed as follows: One half-cell consists of a platinum wire immersed in a solution containing $1.0 \text{ M } \text{Sn}^{2+}$ and $1.0 \text{ M } \text{Sn}^{4+}$; the other half-cell has a thallium rod immersed in a solution of $1.0 \text{ M } \text{Ti}^+$. (a) Write the half-cell reactions and the overall reaction. (b) What is the equilibrium constant at 25°C ? (c) What is the cell voltage if the Ti^+ concentration is increased tenfold? ($E_{\text{Ti}^+|\text{Ti}}^\circ = -0.34 \text{ V}$.)
- 13.95 Given the standard reduction potential for Au^{3+} in Table 13.1 and
- $$\text{Au}^+(\text{aq}) + e^- \longrightarrow \text{Au}(s) \quad E^\circ = 1.69 \text{ V}$$
- answer the following questions. (a) Why does gold not tarnish in air? (b) Will the following disproportionation occur spontaneously?
- $$3\text{Au}^+(\text{aq}) \longrightarrow \text{Au}^{3+}(\text{aq}) + 2\text{Au}(s)$$
- (c) Predict the reaction between gold and fluorine gas.
- 13.96 The ingestion of a very small quantity of mercury is not considered too harmful. Would this statement still hold if the gastric juice in your stomach were mostly nitric acid instead of hydrochloric acid?
- 13.97 When 25.0 mL of a solution containing both Fe^{2+} and Fe^{3+} ions is titrated with 23.0 mL of $0.0200 \text{ M } \text{KMnO}_4$ (in dilute sulfuric acid), all the Fe^{2+} ions

are oxidized to Fe^{3+} ions. Next, the solution is treated with Zn metal to convert all the Fe^{3+} ions to Fe^{2+} ions. Finally, 40.0 mL of the same KMnO_4 solution is added to the solution in order to oxidize the Fe^{2+} ions to Fe^{3+} . Calculate the molar concentrations of Fe^{2+} and Fe^{3+} in the original solution.

- 13.98 Consider the Daniell cell in Figure 13.3. When viewed externally, the anode appears negative and the cathode positive (electrons are flowing from the anode to the cathode). Yet in solution anions are moving toward the anode, which means that it must appear positive to the anions. Because the anode cannot simultaneously be negative and positive, give an explanation for this apparently contradictory situation.

- 13.99 Use the data in Table 13.1 to show that the decomposition of H_2O_2 (a diaproportionation reaction) is spontaneous at 25°C:



- 13.100 Lead storage batteries are rated by ampere hours, that is, the number of amperes they can deliver in an hour. (a) Show that 1 A h = 3600 C. (b) The lead anodes of a certain lead storage battery have a total mass of 406 g. Calculate the maximum theoretical capacity of the battery in ampere-hours. Explain why in practice we can never extract this much energy from the battery. (c) Calculate $\mathcal{E}_{\text{cell}}^{\circ}$ and ΔG° for the battery.

- 13.101 The concentration of sulfuric acid in the lead storage battery of an automobile over a period of time has decreased from 38.0 percent by mass (density = 1.29 g mL^{-1}) to 26.0 percent by mass (1.19 g mL^{-1}). Assume the volume of the acid remains constant at 724 mL. (a) Calculate the total charge in coulombs supplied by the battery. (b) How long (in hours) will it take to recharge the battery back to the original sulfuric acid concentration using a current of 22.4 A.

- 13.102 A spoon was silver-plated electrolytically in an AgNO_3 solution. (a) Sketch a diagram for the process. (b) If 0.884 g of Ag was deposited on the spoon at a constant current of 18.5 mA, how long (in minutes) did the electrolysis take?

- 13.103 Comment on whether F_2 will become a stronger oxidizing agent with increasing H^+ concentration.

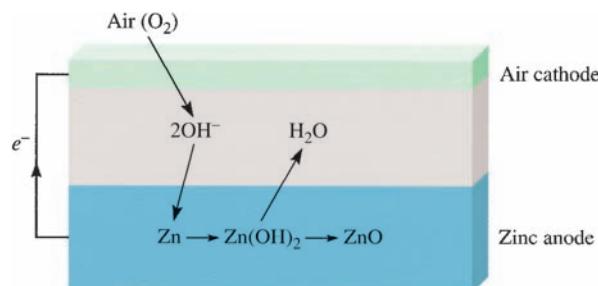
- 13.104 In recent years, there has been much interest in electric cars. List some advantages and disadvantages of electric cars compared to automobiles with internal combustion engines.

- 13.105 Calculate the pressure of H_2 (in bar) required to maintain equilibrium with respect to the following reaction at 25°C:

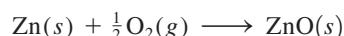


given that $[\text{Pb}^{2+}] = 0.035 \text{ M}$ and the solution is buffered at pH 1.60.

- 13.106 A piece of magnesium ribbon and a copper wire are partially immersed in a 0.1 M HCl solution in a beaker. The metals are joined externally by another piece of metal wire. Bubbles are seen to evolve at both the Mg and Cu surfaces. (a) Write equations representing the reactions occurring at the metals. (b) What visual evidence would you seek to show that Cu is not oxidized to Cu^{2+} ? (c) At some stage, NaOH solution is added to the beaker to neutralize the HCl. Upon further addition of NaOH, a white precipitate forms. What is it?
- 13.107 The zinc-air battery shows much promise for electric cars because it is lightweight and rechargeable:

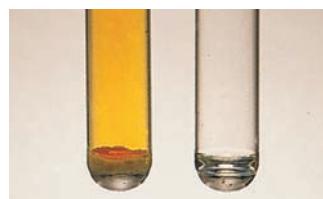


The net transformation is

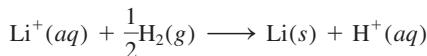


(a) Write the half-reactions at the zinc-air electrodes and calculate the standard emf of the battery at 25°C. (b) Calculate the emf under actual operating conditions when the partial pressure of oxygen is 0.21 bar. (c) What is the energy density (measured as the energy in kilojoules that can be obtained from 1 kg of the metal) of the zinc electrode? (d) If a current of $2.1 \times 10^5 \text{ A}$ is to be drawn from a zinc-air battery system, what volume of air (in liters) would need to be supplied to the battery every second? Assume that the temperature is 25°C and the partial pressure of oxygen is 0.21 bar.

- 13.108 Calculate \mathcal{E}° for the reactions of mercury with (a) 1 M HCl and (b) 1 M HNO_3 . Which acid will oxidize Hg to Hg_2^{2+} under standard-state conditions? Can you identify which test tube below contains HNO_3 and Hg and which contains HCl and Hg ?

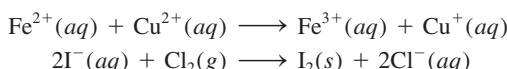


- 13.109** Because all alkali metals react with water, it is not possible to measure the standard reduction potentials of these metals directly as in the case of, say, zinc. An indirect method is to consider the following hypothetical reaction



Use the appropriate equation presented in this chapter and the thermodynamic data in Appendix 2, to calculate \mathcal{E}° for $\text{Li}^+(aq) + e^- \longrightarrow \text{Li}(s)$ at 298 K. Compare your result with that listed in Table 13.1.

- 13.110** Which of the following two redox reactions would you expect to have the largest change in standard emf when the temperature is increased?



Explain your answer.

- 13.111** Compare the pros and cons of a fuel cell, such as the hydrogen-oxygen fuel cell, and a coal-fired station for generating electricity.
- 13.112** Using the data from Table 13.1, calculate the equilibrium constant for the following reaction at 298 K:

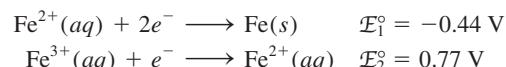


- 13.113** Use Equation 13.6 to calculate the emf values of the Daniel cell at 80°C. Comment on your results. What assumptions are made in this calculation? (*Hint:* Use the thermodynamic data in Appendix 2.)
- 13.114** A construction company is installing an iron culvert (a long cylindrical tube) that is 40.0 m long with a radius of 0.900 m. To prevent corrosion, the culvert must be galvanized. This process is carried out by first passing an iron sheet of appropriate dimensions through an electrolytic cell containing Zn^{2+} ions, using graphite as the anode and the iron sheet as the cathode. If the voltage is 3.26 V, what is the cost of electricity for depositing a layer 0.200 mm thick if the efficiency of the process is 95 percent? The electricity rate is \$0.12 per kilowatt hour (kWh), where 1 W = 1 J s⁻¹, and the density of Zn is 7.14 g cm⁻³.
- 13.115** A 9.00×10^{-2} -mL sample of 0.200 M MgI_2 was electrolyzed. As a result, hydrogen gas was generated

at the cathode and iodine was formed at the anode. The volume of hydrogen collected at 26°C and 779 mmHg was 1.22×10^3 mL. (a) Calculate the charge in coulombs consumed in the process. (b) How long (in min) did the electrolysis last if a current of 7.55 A was used? (c) A white precipitate was formed in the process. What was it, and what was its mass in grams? Assume the volume of the solution was constant.

- 13.116** Assuming that both ΔH° and ΔS° are independent of temperature, derive Equation 13.7 starting from Equation 13.6.

- 13.117** Based on the following standard reduction potentials:



calculate the standard reduction potential for the half-reaction



- 13.118** To remove the tarnish (Ag_2S) on a silver spoon, a student carried out the following steps. First, she placed the spoon in a large pan filled with water so the spoon was totally immersed. Next, she added a few tablespoonful of baking soda (sodium bicarbonate), which readily dissolved. Finally, she placed some aluminum foil at the bottom of the pan in contact with the spoon and then heated the solution to about 80°C. After a few minutes, the spoon was removed and rinsed with cold water. The tarnish was gone and the spoon had regained its original shiny appearance. (a) Describe with equations the electrochemical basis for the procedure. (b) Adding NaCl instead of NaHCO_3 would also work because both compounds are strong electrolytes. What is the added advantage of using NaHCO_3 ? (*Hint:* Consider the pH of the solution.) (c) What is the purpose of heating the solution? (d) Some commercial tarnish removers contain a fluid (or paste) that is a dilute HCl solution. Rubbing the spoon with the fluid will also remove the tarnish. Name two disadvantages of using this procedure compared to the one described.

Answers to Practice Exercises

- 13.1** (a) P + 3, F - 1; (b) Mn + 7, O - 2; (c) Cl + 5, O - 2; and (d) S + 6, F - 1 **13.2** $5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \longrightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}$ **13.3** No **13.4** 0.34 V **13.5** 1×10^{-42}

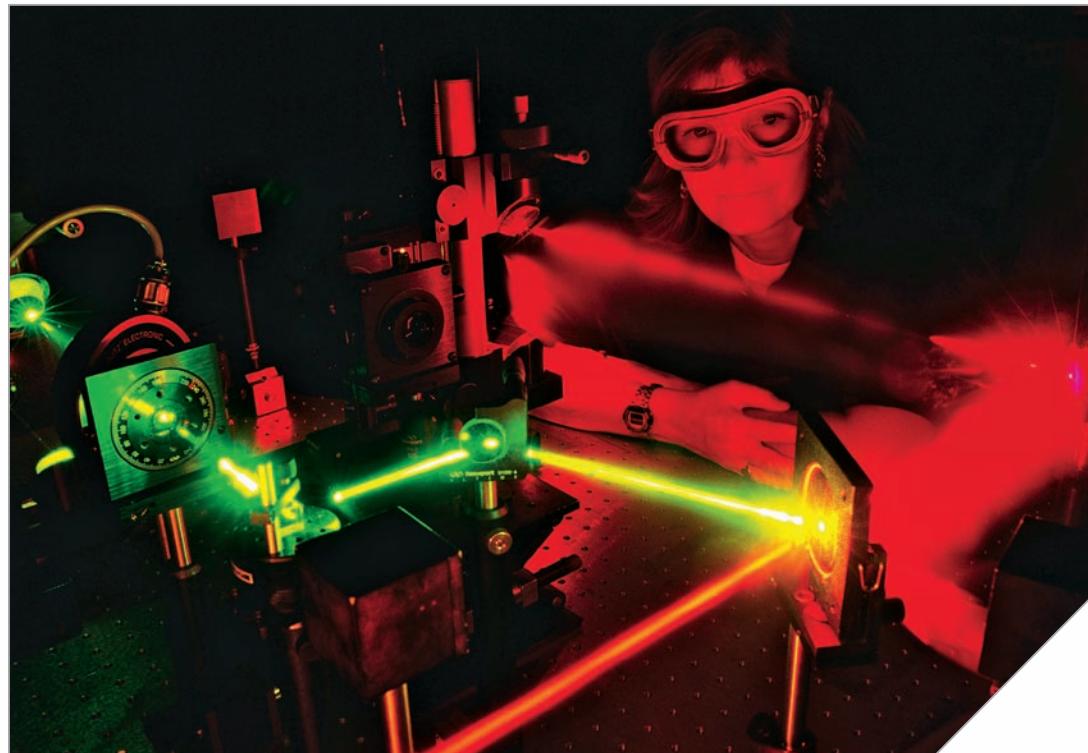
- 13.6** $\Delta G^\circ = -4.1 \times 10^2 \text{ kJ mol}^{-1}$ **13.7** 1.10 V **13.8** Yes, $\mathcal{E} = +0.01 \text{ V}$ **13.9** 0.38 V **13.10** Anode, O_2 ; Cathode, H_2 **13.11** $2.0 \times 10^4 \text{ A}$

14

Chapter

Chemical Kinetics

- 14.1** Chemical Kinetics Is the Study of the Rates at Which Chemical Reactions Occur 713
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14.1 | Chemical Kinetics Is the Study of the Rates at Which Chemical Reactions Occur

The study of chemical equilibrium, explored in Chapters 10–13, can determine whether a particular reaction is possible under the given conditions and how far that reaction will proceed before equilibrium is reached. However, the laws of chemical thermodynamics and the principles of chemical equilibrium cannot determine how fast a reaction will proceed. The speed of a chemical reaction is obtained through the study of **chemical kinetics**, which is *the area of chemistry concerned with the rates at which chemical reactions occur*. The word *kinetic* suggests movement or change; recall from Chapter 5 that kinetic energy is the energy available because of the motion of an object. Here “kinetics” refers to the **reaction rate**, which is *the change in the concentration of a reactant or a product with time ($M\ s^{-1}$)*.

Rates of Reaction

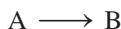
There are many reasons for studying the rate of a reaction. To begin with, there is an intrinsic curiosity about why reactions have such vastly different rates. Some processes, such as the initial steps in vision and photosynthesis and nuclear chain reactions, take place on a time scale as short as 10^{-12} to 10^{-6} s. Others, like the curing of cement and the conversion of graphite to diamond, take years or millions of years to complete. On a practical level, a knowledge of reaction rates is useful in drug design, pollution control, and food processing. Industrial chemists often place more emphasis on speeding up the rate of a reaction than they do on maximizing its yield.

Any chemical reaction can be represented by the general equation



This equation tells us that during the course of a reaction, reactants are consumed while products are formed. As a result, we can follow the progress of a reaction by monitoring either the decrease in concentration of the reactants or the increase in concentration of the products.

Figure 14.1 shows the progress of a simple reaction in which molecules of A (gray spheres) are converted to molecules of B (red spheres):



The decrease in the number of A molecules and the increase in the number of B molecules with time are graphed in Figure 14.2.

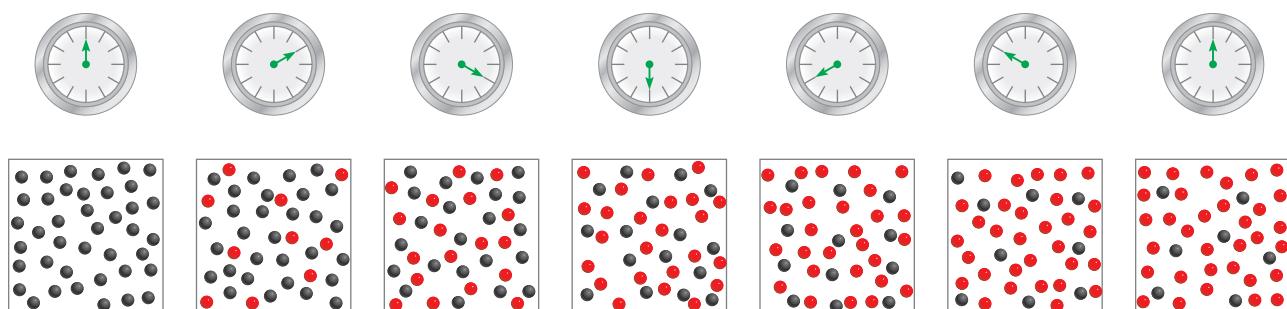
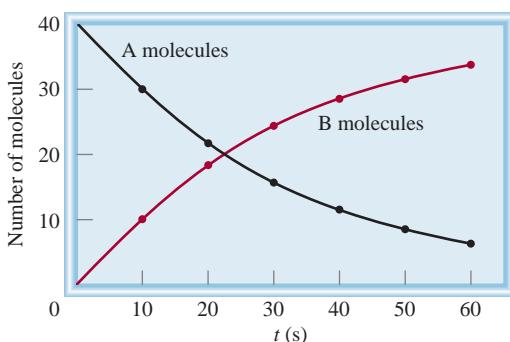


Figure 14.1 The progress of reaction $\text{A} \longrightarrow \text{B}$ at 10-s intervals over a period of 60 s. Initially, only molecules of A (gray spheres) are present. As time progresses, B molecules (red spheres) are formed.

Figure 14.2 The rate of reaction $A \longrightarrow B$, represented as the decrease of A molecules with time and as the increase of B molecules with time.



In general, it is more convenient to express the reaction rate in terms of the change in concentration with time. Thus, for the reaction $A \longrightarrow B$, we can express the *average* rate over a time interval $\Delta t = t_2 - t_1$ as

$$\text{average rate} = -\frac{[A]_{t_2} - [A]_{t_1}}{t_2 - t_1} = -\frac{\Delta[A]}{\Delta t}$$

where $\Delta[A]$ represents the change in the concentration (molarity) of A over the time interval. Because the concentration of reactant A *decreases* during the time interval, $\Delta[A]$ is a negative quantity. The rate of a reaction is a positive quantity, so a minus sign is needed in the rate expression to make the rate positive. The rate can also be defined in terms of the rate of production of the product B:

$$\text{average rate} = \frac{[B]_{t_2} - [B]_{t_1}}{t_2 - t_1} = \frac{\Delta[B]}{\Delta t}$$

where no minus sign is required because $\Delta[B]$ is a positive quantity (the concentration of B *increases* with time).

In practice, we find that the quantity of interest is not the rate over a certain time interval (because this is only an average quantity whose value depends on the particular value of Δt); rather, we are interested in the instantaneous rate. In the language of calculus, as Δt becomes smaller and eventually approaches zero, the *instantaneous rate* of the reaction at a specific time t can be defined as

$$\text{instantaneous rate} = -\frac{d[A]}{dt} = +\frac{d[B]}{dt}$$

Using this definition, we do not need to worry about what time interval is used. Unless otherwise stated, we will refer to the instantaneous rate merely as “the rate.”

To determine the rate of a reaction experimentally, we have to monitor the concentration of the reactant (or product) as a function of time. For reactions in solution, the concentration of a species can often be measured by spectroscopic means. If ions are involved, the change in concentration can also be detected by an electrical conductance measurement. Reactions involving gases are most conveniently followed by pressure measurements. We will consider two specific reactions for which different methods are used to measure the reaction rate.

Reaction of Bromine and Formic Acid

Consider, for example, the reaction of molecular bromine (Br_2) with formic acid (HCOOH) in aqueous solution:





Figure 14.3 The decrease in bromine concentration as time elapses shows up as a loss of color (from left to right).

Molecular bromine is reddish-brown in color. All the other species in the reaction are colorless. As the reaction progresses, the concentration of Br_2 steadily decreases and its color fades (Figure 14.3). This loss of color and hence concentration can be monitored easily with a spectrometer, which registers the amount of visible light absorbed by bromine (Figure 14.4).

Measuring the change (decrease) in bromine concentration at some initial time and then at some final time enables us to determine the average rate of the reaction during that interval:

$$\text{average rate} = -\frac{\Delta[\text{Br}_2]}{\Delta t} = -\frac{[\text{Br}_2]_{t_2} - [\text{Br}_2]_{t_1}}{t_2 - t_1}$$

The data in Table 14.1 show the experimental bromine concentration as a function of time for a reaction of Br_2 with a large excess of formic acid in aqueous solution. From these data, we can calculate the average rate over the first 50-s time interval as follows:

$$\text{average rate} = -\frac{(0.0101 - 0.0120) M}{50.0 \text{ s}} = 3.8 \times 10^{-5} M \text{ s}^{-1}$$

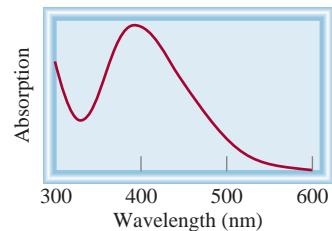
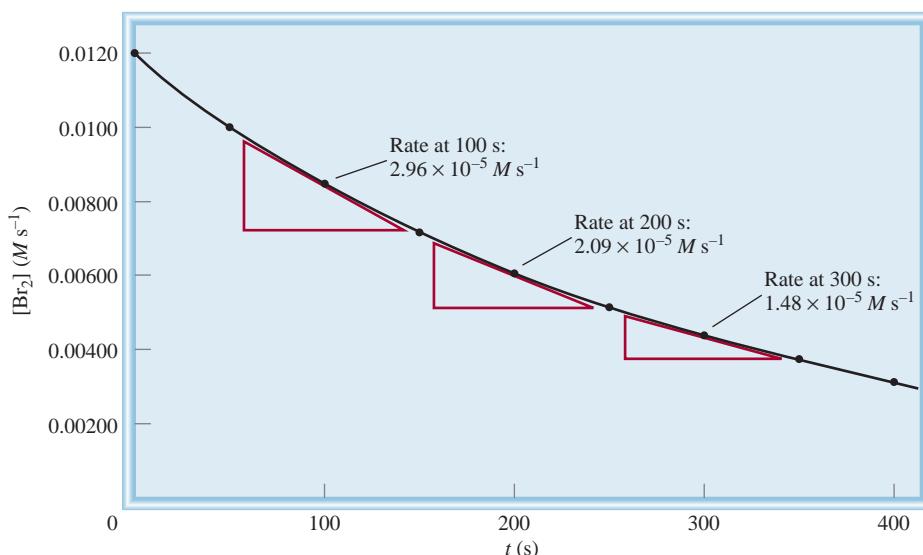


Figure 14.4 Plot of absorption of bromine versus wavelength. The maximum absorption of visible light by bromine occurs at 393 nm. As the reaction progresses, the absorption, which is proportional to $[\text{Br}_2]$, decreases with time, indicating a depletion in bromine.

Table 14.1 Measured Rates for the Reaction Between Molecular Bromine and Formic Acid at 25°C

| Time (s) | $[\text{Br}_2] (M)$ | Instantaneous Rate ($M \text{ s}^{-1}$) | $k = \frac{\text{rate}}{[\text{Br}_2]} (\text{s}^{-1})$ |
|----------|---------------------|---|---|
| 0.0 | 0.0120 | 4.20×10^{-5} | 3.50×10^{-3} |
| 50.0 | 0.0101 | 3.52×10^{-5} | 3.49×10^{-3} |
| 100.0 | 0.00846 | 2.96×10^{-5} | 3.50×10^{-3} |
| 150.0 | 0.00710 | 2.49×10^{-5} | 3.51×10^{-3} |
| 200.0 | 0.00596 | 2.09×10^{-5} | 3.51×10^{-3} |
| 250.0 | 0.00500 | 1.75×10^{-5} | 3.50×10^{-3} |
| 300.0 | 0.00420 | 1.48×10^{-5} | 3.52×10^{-3} |
| 350.0 | 0.00353 | 1.23×10^{-5} | 3.48×10^{-3} |
| 400.0 | 0.00296 | 1.04×10^{-5} | 3.51×10^{-3} |

Figure 14.5 The instantaneous rates of the reaction between molecular bromine and formic acid at $t = 100$ s, 200 s, and 300 s are given by the derivative (the slope of the tangent lines) at each time.



If we had chosen the first 100 s as our time interval, the average rate would then be given by:

$$\text{average rate} = -\frac{(0.00846 - 0.0120) M}{100.0 \text{ s}} = 3.54 \times 10^{-5} \text{ M s}^{-1}$$

These calculations demonstrate that the average rate of the reaction depends on the time interval we choose. By calculating the average reaction rate over shorter and shorter intervals, we can obtain the instantaneous rate of the reaction at each time (see Table 14.1). Figure 14.5 shows the plot of $[Br_2]$ versus time, based on the data listed in Table 14.1. Graphically, the instantaneous rate at a given time is given by the derivative of the curve (the slope of the tangent line) with respect to time (see Appendix 1). The instantaneous rate will always have the same value for the same concentrations of reactants, as long as the temperature is kept constant.

The rate of the bromine–formic acid reaction also depends on the concentration of formic acid. However, by adding a large excess of formic acid to the reaction mixture, we can ensure that the concentration of formic acid remains virtually constant throughout the course of the reaction. Under this condition the change in the amount of formic acid present in solution has no effect on the measured rate.

What effect does the bromine concentration have on the rate of reaction? According to Table 14.1, the bromine concentration is 0.0101 M at $t = 50 \text{ s}$ and the rate of the reaction is $3.52 \times 10^{-5} \text{ M s}^{-1}$. At $t = 250 \text{ s}$, the bromine concentration is 0.00500 M and the rate of reaction is $1.75 \times 10^{-5} \text{ M s}^{-1}$. The concentration at $t = 50 \text{ s}$ is double the concentration at $t = 250 \text{ s}$ (0.0101 M versus 0.00500 M), and the rate of reaction at $t = 50 \text{ s}$ is double the rate at $t = 250 \text{ s}$ ($3.52 \times 10^{-5} \text{ M s}^{-1}$ versus $1.75 \times 10^{-5} \text{ M s}^{-1}$). In other words, the rate of reaction doubles as the concentration of bromine doubles. The rate is directly proportional to the Br_2 concentration:

$$\begin{aligned}\text{rate} &\propto [Br_2] \\ &= k[Br_2]\end{aligned}$$

The symbol “ \propto ” means “is proportional to”.

where the term k is known as the **rate constant**—a constant of proportionality between the reaction rate and the concentration of reactant.

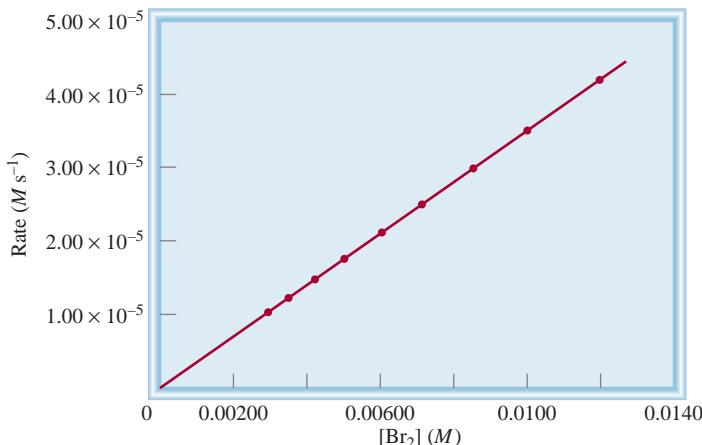


Figure 14.6 Plot of the rate versus molecular bromine concentration for the reaction between molecular bromine and formic acid. The straight-line relationship shows that the rate of reaction is directly proportional to the molecular bromine concentration.

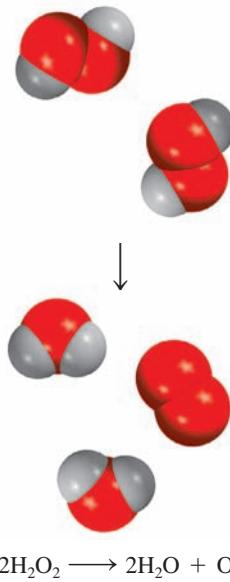


Figure 14.6 is a plot of the rate versus Br_2 concentration. The graph is a straight line because the rate is directly proportional to the concentration; the higher the concentration, the higher the rate. Rearranging the last equation gives

$$k = \frac{\text{rate}}{[\text{Br}_2]}$$

Because reaction rate has the units $M \text{ s}^{-1}$, and $[\text{Br}_2]$ has units of M , the unit of k is s^{-1} in this case. The rate constant (k) is *unaffected* by the concentration of Br_2 . The rate is greater at a higher concentration and smaller at a lower concentration of Br_2 , but the *ratio* of rate/ $[\text{Br}_2]$ remains the same provided the temperature does not change.

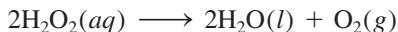
From Table 14.1, we can calculate the rate constant for the reaction. Taking the data for $t = 50$ s, we write

$$k = \frac{\text{rate}}{[\text{Br}_2]} = \frac{3.52 \times 10^{-5} \text{ M s}^{-1}}{0.0101 \text{ M}} = 3.49 \times 10^{-3} \text{ s}^{-1}$$

We can use the data for any t to calculate k . The slight variations in the values of k listed in Table 14.1 are due to experimental deviations in the rate measurements.

Decomposition of Hydrogen Peroxide

If one of the products or reactants is a gas, we can use a manometer to find the reaction rate. Consider, for example, the decomposition of hydrogen peroxide at 20°C:



In this case, the rate of decomposition can be determined by monitoring the rate of oxygen evolution with a manometer (Figure 14.7).

The oxygen partial pressure can be readily converted to concentration by using the ideal gas equation:

$$P_{\text{O}_2}V = n_{\text{O}_2}RT$$

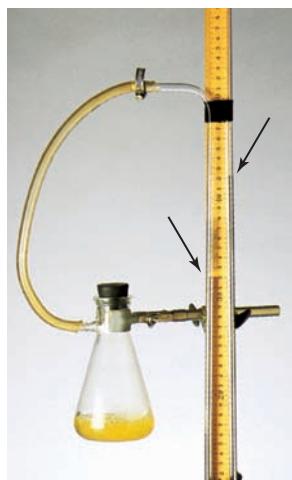
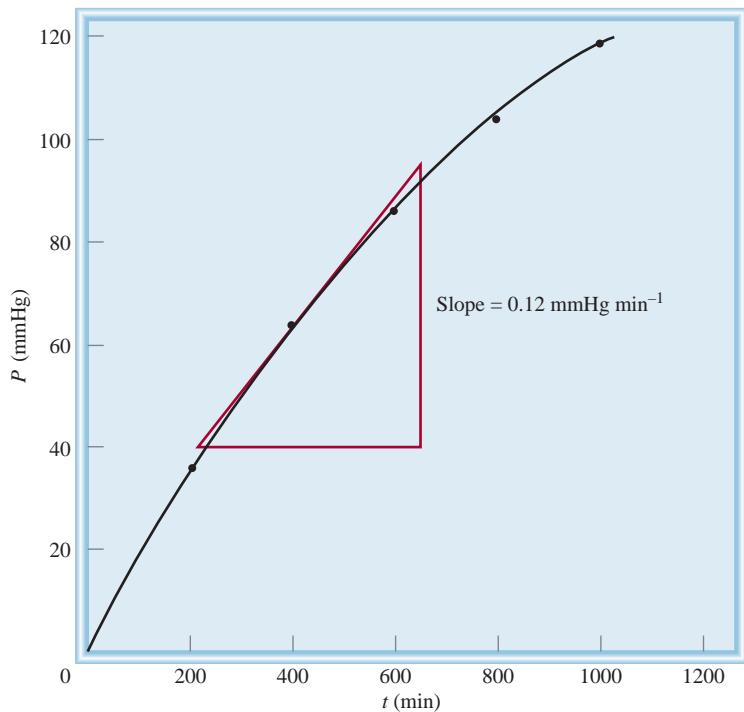


Figure 14.7 The rate of hydrogen peroxide decomposition can be measured with a manometer, which shows the increase in the oxygen gas pressure with time. The arrows show the mercury levels in the *U* tube.

Figure 14.8 The instantaneous rate for the decomposition of hydrogen peroxide at 400 min is given by the slope of the tangent multiplied by $1/RT$.



or

$$P_{O_2} = \frac{n_{O_2} RT}{V} = [O_2]RT$$

where n_{O_2}/V gives the molarity of oxygen gas. Rearranging the equation, we get

$$[O_2] = \frac{1}{RT} P_{O_2}$$

The reaction rate, which is given by the rate of oxygen production, can now be written as

$$\text{rate} = -\frac{d[O_2]}{dt} = \frac{-1}{RT} \frac{dP_{O_2}}{dt}$$

Figure 14.8 shows the increase in oxygen pressure with time and the determination of an instantaneous rate at 400 min. To express the rate in the usual units of $M s^{-1}$, we convert mmHg min^{-1} to bar s^{-1} and then multiply the slope of the tangent (dP_{O_2}/dt) by $1/RT$, as shown in the preceding equation.

Reaction Rates and Stoichiometry

We have just seen that for stoichiometrically simple reactions of the type $A \longrightarrow B$, the rate can be expressed in terms of the decrease in reactant concentration with time, $-d[A]/dt$, or the increase in product concentration with time, $d[B]/dt$. Now consider the slightly more complex reaction:



Two moles of A disappear for each mole of B that forms, that is, the rate of disappearance of A is twice as fast as the rate of appearance of B. The rate can be written as either

$$\text{rate} = -\frac{1}{2} \frac{d[A]}{dt} \quad \text{or} \quad \text{rate} = +\frac{d[B]}{dt}$$

In general, for the reaction



the rate is given by

$$\text{rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt} \quad (14.1)$$

Example 14.1 shows how to write reaction rate expressions and calculate rates of product formation and reactant disappearance.

Example 14.1

Consider the reaction $4\text{NO}_2(g) + \text{O}_2(g) \longrightarrow 2\text{N}_2\text{O}_5(g)$. Suppose that, at a particular moment during the reaction, N_2O_5 is being formed at a rate of 0.048 M s^{-1} . (a) Write the rate expression in terms of the disappearance of the reactants, NO_2 and O_2 , and the appearance of the product, N_2O_5 . (b) What is the overall rate? (c) At what rate is O_2 reacting? (d) At what rate is NO_2 reacting?

Solution (a) Using Equation 14.1, we have

$$\text{rate} = -\frac{1}{4} \frac{d[\text{NO}_2]}{dt} = -\frac{d[\text{O}_2]}{dt} = +\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt}$$

(b) We are given

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = 0.048 \text{ M s}^{-1}$$

From the rate expression,

$$\text{rate} = \frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{2} (0.048 \text{ M s}^{-1}) = 0.024 \text{ M s}^{-1}$$

(c) From part (a), $\text{rate} = -\frac{d[\text{O}_2]}{dt}$ and from part (b), $\text{rate} = 0.024 \text{ M s}^{-1}$, so

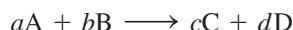
$$\frac{d[\text{O}_2]}{dt} = -\text{rate} = -0.024 \text{ M s}^{-1}$$

(d) From part (a) $\frac{d[\text{NO}_2]}{dt} = -4 \times \text{rate} = -4 \times (0.024 \text{ M s}^{-1}) = -0.096 \text{ M s}^{-1}$

Practice Exercise Consider the reaction $4\text{PH}_3(g) \longrightarrow \text{P}_4(g) + 6\text{H}_2(g)$. Suppose that, at a particular moment during the reaction, molecular hydrogen is being formed at the rate of 0.078 M s^{-1} . (a) What is the overall rate of the reaction? (b) At what rate is P_4 being formed? (c) At what rate is PH_3 reacting?

14.2 | The Rate Law Gives the Dependence of the Reaction Rate on the Reactant Concentrations

So far we have learned that the rate of a reaction is proportional to the concentration of reactants and that the proportionality constant k is called the rate constant. The *rate law* expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers. For the general reaction



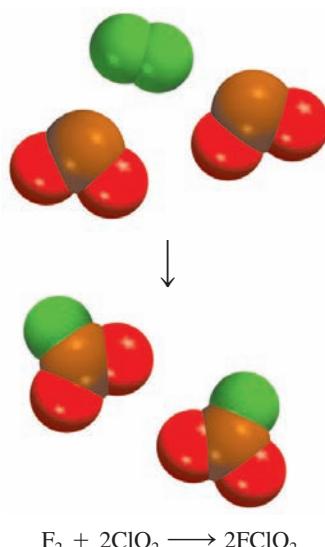
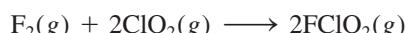
the rate law takes the form

$$\text{rate} = k[A]^x[B]^y \quad (14.2)$$

where x and y are numbers that must be determined experimentally. The exponents x and y are *not necessarily* equal to the stoichiometric coefficients a and b and must be obtained from experiment. When we know the values of x , y , and k , we can use Equation 14.2 to calculate the rate of the reaction, given the concentrations of A and B.

The exponents x and y specify the relationships between the concentrations of reactants A and B and the reaction rate. Added together, they give us the overall **reaction order**, defined as *the sum of the powers to which all reactant concentrations appearing in the rate law are raised*. For Equation 14.2, the overall reaction order is $x + y$. Alternatively, we can say that the reaction is x^{th} order in A, y^{th} order in B, and $(x + y)^{\text{th}}$ order overall.

To see how to determine the rate law of a reaction, consider the following reaction between fluorine and chlorine dioxide:



One way to study the effect of reactant concentration on reaction rate is to determine how the *initial rate* depends on the starting concentrations. It is preferable to measure the initial rates because, as the reaction proceeds, the concentrations of the reactants decrease and it may become difficult to measure the changes accurately. Also, there may be a reverse reaction of the type



which would introduce error into the rate measurement. Both of these complications are virtually absent during the early stages of the reaction.

Table 14.2 lists three rate measurements for the formation of FCLO_2 . According to entries 1 and 3, the reaction rate doubles if we double $[F_2]$ while holding $[\text{ClO}_2]$ constant. Thus, the rate is directly proportional to $[F_2]$. Similarly, the data in entries

Table 14.2 Rate Data for the Reaction between F_2 and ClO_2

| $[\text{F}_2] \text{ (M)}$ | $[\text{ClO}_2] \text{ (M)}$ | Initial Rate ($M \text{ s}^{-1}$) |
|----------------------------|------------------------------|-------------------------------------|
| 1. 0.10 | 0.010 | 1.2×10^{-3} |
| 2. 0.10 | 0.040 | 4.8×10^{-3} |
| 3. 0.20 | 0.010 | 2.4×10^{-3} |

1 and 2 show that the rate quadruples if we quadruple $[ClO_2]$ at constant $[F_2]$. Thus, the rate is also directly proportional to $[ClO_2]$. We can summarize our observations by writing the rate law as

$$\text{rate} = k[F_2][ClO_2]$$

Because both $[F_2]$ and $[ClO_2]$ are raised to the first power, the reaction is first order in F_2 , first order in ClO_2 , and second order ($1 + 1 = 2$) overall. Note that $[ClO_2]$ is raised to the power of 1 in the rate equation, whereas its stoichiometric coefficient in the overall chemical equation is 2. For F_2 , the reaction order (first) and stoichiometric coefficient (1) for F_2 are coincidentally the same.

From the reactant concentrations and the initial rate, we can also calculate the rate constant. Using the first entry of data in Table 14.2, we can write

$$\begin{aligned} k &= \frac{\text{rate}}{[F_2][ClO_2]} \\ &= \frac{1.2 \times 10^{-3} M s^{-1}}{(0.10 M)(0.010 M)} \\ &= 1.2 M^{-1} s^{-1} \end{aligned}$$

The units of k depend upon the overall order of the reaction. For this second-order reaction they are $M^{-1} s^{-1}$. For a first-order reaction, the units of k are s^{-1} . In general the units for k for an n^{th} -order reaction are $M^{1-n} s^{-1}$.

Knowing the reaction order enables us to understand how the reaction depends on reactant concentration. Suppose, for example, that the general reaction



is first order in A and second order in B (that is, $x = 1$ and $y = 2$ in Equation 14.2). The rate law for the reaction is

$$\text{rate} = k[A][B]^2$$

This reaction is third order overall ($1 + 2 = 3$). Let us assume that initially $[A] = 1.0 M$ and $[B] = 1.0 M$. The rate law tells us that if we double the concentration of A from $1.0 M$ to $2.0 M$ at constant $[B]$, we also double the reaction rate. On the other hand, if we double the concentration of B from $1.0 M$ to $2.0 M$ at constant $[A] = 1 M$, the rate will increase by a factor of four because of the power of two in the exponent.

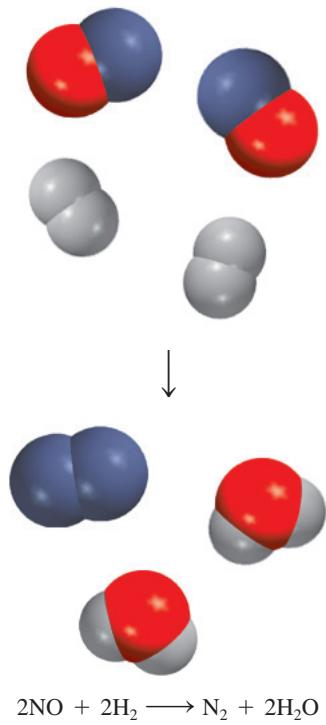
If for another reaction $x = 0$ and $y = 1$, then the rate law is

$$\text{rate} = k[A]^0[B]^1 = k[B]$$

This reaction is zero order in A, first order in B, and first order overall. The exponent zero tells us that the rate of this reaction is *independent* of the concentration of A. Although we have only discussed reactions so far for which the reaction orders are whole numbers, reaction orders can also be fractional. In summary,

1. Rate laws are always determined experimentally. From the concentration of reactants and the initial reaction rates, we can determine the reaction order and then the rate constant of the reaction.
2. Reaction order is always defined in terms of reactant (not product) concentrations.
3. The order of a reactant is unrelated to the stoichiometric coefficient of the reactant in the overall balanced equation and must be determined from experiment.

Example 14.2 illustrates the procedure for determining the rate law of a reaction.

**Example 14.2**

The reaction of nitric oxide with hydrogen at 1280°C is



From the following data collected at this temperature, determine (a) the rate law, (b) the rate constant, and (c) the rate of the reaction when [NO] = 13.0 × 10⁻³ M and [H₂] = 6.0 × 10⁻³ M.

| Experiment | [NO] (M) | [H ₂] (M) | Initial Rate (M s ⁻¹) |
|------------|-------------------------|------------------------|-----------------------------------|
| 1 | 10.0 × 10 ⁻³ | 2.0 × 10 ⁻³ | 5.0 × 10 ⁻⁵ |
| 2 | 10.0 × 10 ⁻³ | 4.0 × 10 ⁻³ | 10.0 × 10 ⁻⁵ |
| 3 | 14.0 × 10 ⁻³ | 2.0 × 10 ⁻³ | 9.8 × 10 ⁻⁵ |

Strategy We are given a set of concentration and reaction rate data and asked to determine the rate law and the rate constant. We assume that the rate law takes the form

$$\text{rate} = k[\text{NO}]^x[\text{H}_2]^y$$

We need to compare the data from the different experiments to determine *x* and *y*. Once the orders of the reactants are known, we can calculate *k* from any set of rates and concentrations. Finally, the rate law enables us to calculate the rate at any concentrations of NO and H₂.

Solution (a) Experiments 1 and 2 show that the rate doubles when we double the concentration of H₂ at constant concentration of NO. Therefore, the rate law is first order in H₂ and *y* = 1.

Experiments 1 and 3 indicate that increasing [NO] from 10.0 × 10⁻³ M to 14.0 × 10⁻³ M at constant [H₂] increases the rate from 5.0 × 10⁻⁵ M s⁻¹ to 9.8 × 10⁻⁵ M s⁻¹. Because the concentration is not increased by a simple integer factor, determining the power *x* is more complex and must be determined using logarithms. Using the rate law (with *y* = 1), the ratio of the rate in experiment 3 to that of experiment 1 is given by

$$\frac{\text{rate 3}}{\text{rate 1}} = \frac{k[\text{NO}]_{\text{exp 3}}^x [\text{H}_2]_{\text{exp 3}}^1}{k[\text{NO}]_{\text{exp 1}}^x [\text{H}_2]_{\text{exp 1}}^1}$$

$$\frac{9.8 \times 10^{-5} \text{ M s}^{-1}}{5.0 \times 10^{-5} \text{ M s}^{-1}} = \frac{(14.0 \times 10^{-3} \text{ M})^x (2.0 \times 10^{-3} \text{ M})}{(10.0 \times 10^{-3} \text{ M})^x (2.0 \times 10^{-3} \text{ M})}$$

$$1.96 = 1.4^x$$

Taking the natural log of both sides gives

$$\ln(1.96) = \ln(1.4)^x = x \times \ln(1.4)$$

$$0.673 = x \times 0.336$$

$$x = \frac{0.673}{0.336} = 2.00$$

so the reaction is second order in [NO]. Hence the rate law is given by

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

and the reaction is third order (2 + 1 = 3) overall.

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- (b) The rate constant k can be calculated using the data from any one of the experiments. Rearranging the rate law, we get

$$k = \frac{\text{rate}}{[\text{NO}]^2[\text{H}_2]}$$

The data from experiment 2 give us

$$\begin{aligned} k &= \frac{5.0 \times 10^{-5} \text{ M s}^{-1}}{(10.0 \times 10^{-3} \text{ M})^2 (2.0 \times 10^{-3} \text{ M})} \\ &= 2.5 \times 10^2 \text{ M}^{-2} \text{ s}^{-1} \end{aligned}$$

- (c) Using the known rate constant and the given concentrations of NO and H₂, we write

$$\begin{aligned} \text{rate} &= k[\text{NO}]^2[\text{H}_2] \\ &= (2.5 \times 10^2 \text{ M}^{-2} \text{ s}^{-1})(13.0 \times 10^{-3} \text{ M})^2 (6.0 \times 10^{-3} \text{ M}) \\ &= 2.5 \times 10^{-4} \text{ M s}^{-1} \end{aligned}$$

Comment The reaction is first order in H₂, whereas the stoichiometric coefficient for H₂ in the balanced equation is 2. The order of a reactant is unrelated to its stoichiometric coefficient in the overall balanced equation.

Practice Exercise The reaction of peroxydisulfate ion (S₂O₈²⁻) with iodide ion (I⁻) is



From the following data collected at a certain temperature, determine the rate law and calculate the rate constant at that temperature.

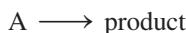
| Experiment | [S ₂ O ₈ ²⁻] (M) | [I ⁻] (M) | Initial Rate (M s ⁻¹) |
|------------|--|-----------------------|-----------------------------------|
| 1 | 0.080 | 0.034 | 2.2 × 10 ⁻⁴ |
| 2 | 0.080 | 0.017 | 1.1 × 10 ⁻⁴ |
| 3 | 0.190 | 0.025 | 3.8 × 10 ⁻⁴ |

14.3 | Integrated Rate Laws Specify the Relationship Between Reactant Concentration and Time

Rate law expressions enable us to calculate the rate of a reaction from the rate constant and reactant concentrations. Using calculus, the rate laws can be transformed by the process of integration to give **integrated rate laws**, which tell us the concentrations of reactants at any time during the course of a reaction. We will illustrate these important concepts by considering two of the simplest kinds of rate laws—those applying to reactions that are first order overall and those applying to reactions that are second order overall.

First-Order Reactions

A **first-order reaction** is a reaction whose rate depends on the reactant concentration raised to the first power. In a first-order reaction of the type



the rate law is

$$\text{rate} = -\frac{d[A]}{dt} = k[A] \quad (14.3)$$

where k is the first-order rate constant. The units of k are s^{-1} . Rearranging Equation 14.3 gives

$$\frac{1}{[A]} d[A] = -k dt \quad (14.4)$$

The time dependence of $[A]$ can be determined using calculus (see Appendix 1). Integrating Equation 14.4 from the initial concentration $[A]_0$ at $t = 0$, to the final concentration $[A]_t$ at $t = t$, we obtain

$$\int_{[A]_0}^{[A]_t} \frac{1}{[A]} d[A] = - \int_0^t k dt$$

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad (14.5)$$

or

$$[A]_t = [A]_0 e^{-kt} \quad (14.6)$$

The time $t = 0$ need not correspond to the beginning of the experiment; it can be any time when we choose to start monitoring the change in the concentration of A. The exponential decay with time indicated by Equation 14.6 is a signature of first-order reactions [Figure 14.9(a)].

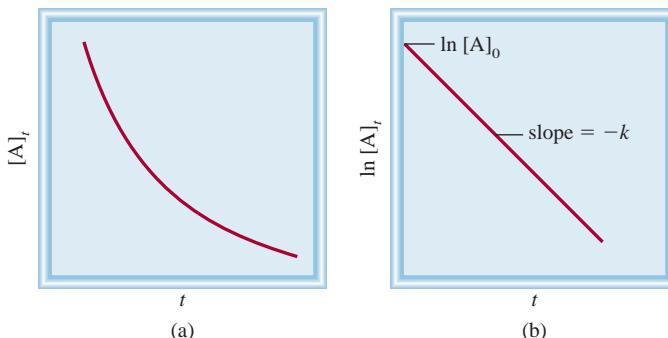
Equation 14.5 can be rearranged as follows

$$\ln \left(\frac{[A]_t}{c_0} \right) = -kt + \ln \left(\frac{[A]_0}{c_0} \right) \quad (14.7)$$

where c_0 is some reference concentration,¹ usually 1 M. Equation 14.7 has the form of a linear equation $y = mx + b$, where m is the slope of the line and b is the y-axis

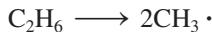
1. The reference concentration, c_0 , is necessary in Equation 14.7 because a quantity must be dimensionless in order to take its natural logarithm. As long as the same reference concentration is used for both $[A]$ and $[A]_0$, the choice of c_0 is arbitrary.

Figure 14.9 The time dependence of reactant concentration for a first-order reaction. (a) A plot of reactant concentration versus time showing the exponential decay of Equation 14.6. (b) A log-linear plot of reactant concentration versus time gives a straight line (Equation 14.7) with a slope of $-k$ and an intercept of $\ln[A]_0$.

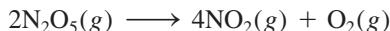


intercept. Thus, for a first-order reaction, a plot of $\ln([A]_t/c_0)$ versus time (t) will be linear with a slope of $-k$ and have a y -axis intercept of $\ln([A]_0/c_0)$. From a graph of this kind, illustrated in Figure 14.9(b), we can determine the rate constant from its slope.

First-order reactions are common. An example is the decomposition of ethane (C_2H_6) into highly reactive fragments called methyl radicals ($CH_3\cdot$):



The decomposition of N_2O_5 is also a first-order reaction

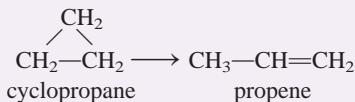


Besides chemical reactions, a number of nonchemical processes in nature also obey first-order kinetics. A particularly important example is radioactive decay, which is discussed in Chapter 17.

In Example 14.3, we apply Equations 14.5 and 14.6 to an organic reaction.

Example 14.3

The conversion of cyclopropane to propene in the gas phase is a first-order reaction with a rate constant of $6.7 \times 10^{-4} \text{ s}^{-1}$ at 500°C .

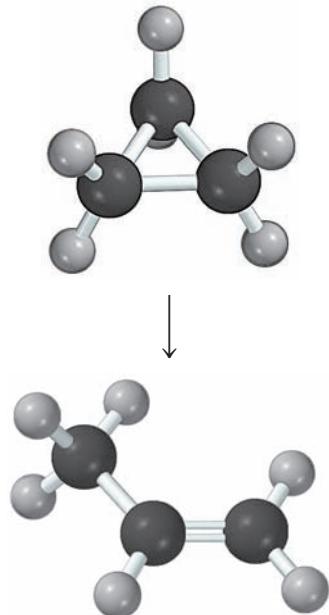


- (a) If the initial concentration of cyclopropane was $0.25 M$, what is the concentration after 8.8 min? (b) How long (in minutes) will it take for the concentration of cyclopropane to decrease from $0.25 M$ to $0.15 M$? (c) How long (in minutes) will it take to convert 74 percent of the starting material?

Strategy The relationship between the concentrations of a reactant at different times in a first-order reaction is given by Equation 14.5 or 14.6. In part (a), we are given $[A]_0$ and t and asked to find $[A]_t$, which can be accomplished by a straightforward substitution into Equation 14.6. In part (b), we are given $[A]_0$ and $[A]_t$, and we are asked to find t . Equation 14.5 contains all these variables, but it must first be rearranged to isolate t on one side. In part (c), we are not given $[A]_t$ and $[A]_0$. However, if initially we have 100 percent of the compound and 74 percent has reacted, then what is left must be $(100\% - 74\%)$, or 26 percent. Thus, the ratio $[A]_t/[A]_0$, which is all we need to determine the time, is equal to 0.26.

Solution (a) In applying Equation 14.6, note that k is given in units of s^{-1} , so we must convert 8.8 min to seconds in the calculation:

$$\begin{aligned} [A]_t &= [A]_0 e^{-kt} \\ &= 0.25 M \times \exp\left[-(6.7 \times 10^{-4} \text{ s}^{-1})(8.8 \text{ min})\left(\frac{60 \text{ s}}{1 \text{ min}}\right)\right] \\ &= 0.25 M \times 0.702 \\ &= 0.18 M \end{aligned}$$



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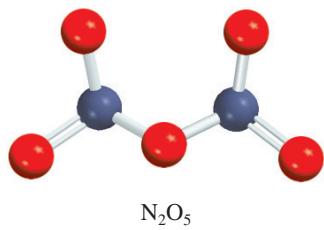
(b) Rearranging Equation 14.5 to isolate t gives

$$\begin{aligned} t &= -k^{-1} \ln \frac{[A]_t}{[A]_0} \\ &= -(6.7 \times 10^{-4} \text{ s}^{-1})^{-1} \ln \frac{0.15 \text{ M}}{0.25 \text{ M}} \\ &= 760 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \\ &= 13 \text{ min} \end{aligned}$$

(c) Using the rearranged Equation 14.5 given in part (b) and the fact that $[A]_t/[A]_0 = 0.26$, we have

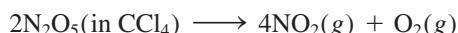
$$\begin{aligned} t &= -k^{-1} \ln \frac{[A]_t}{[A]_0} \\ &= -(6.7 \times 10^{-4} \text{ s}^{-1})^{-1} \ln (0.26) \\ &= 2.0 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \\ &= 33 \text{ min} \end{aligned}$$

Practice Exercise The reaction $2\text{A} \longrightarrow \text{B}$ is first order in A with a rate constant of $2.8 \times 10^{-2} \text{ s}^{-1}$ at 80°C . (a) How long (in seconds) will it take for A to decrease from 0.88 M to 0.14 M ? (b) Assuming that the initial concentration of [A] is 0.90 M and that the initial concentration of [B] is zero, how much time is necessary for the concentration of [B] to reach 0.25 M ?



N_2O_5 decomposes to give NO_2 (brown color).

Now let us determine graphically the order and rate constant of the decomposition of nitrogen pentoxide (N_2O_5) in carbon tetrachloride (CCl_4) solvent at 45°C :



The table shows the variation of N_2O_5 concentration with time, and the corresponding $\ln ([\text{N}_2\text{O}_5])$ values:

| t (s) | $[\text{N}_2\text{O}_5]$ (M) | $\ln ([\text{N}_2\text{O}_5]/1 \text{ M})$ |
|---------|------------------------------|--|
| 0 | 0.91 | -0.094 |
| 300 | 0.75 | -0.29 |
| 600 | 0.64 | -0.45 |
| 1200 | 0.44 | -0.82 |
| 3000 | 0.16 | -1.83 |

Applying Equation 14.7, we plot $\ln ([\text{N}_2\text{O}_5]/1 \text{ M})$ versus t , as shown in Figure 14.10. Because this plot is linear, the rate law must be first order in $[\text{N}_2\text{O}_5]$. Next, there are several ways to estimate the rate constant from the slope, depending upon the accuracy

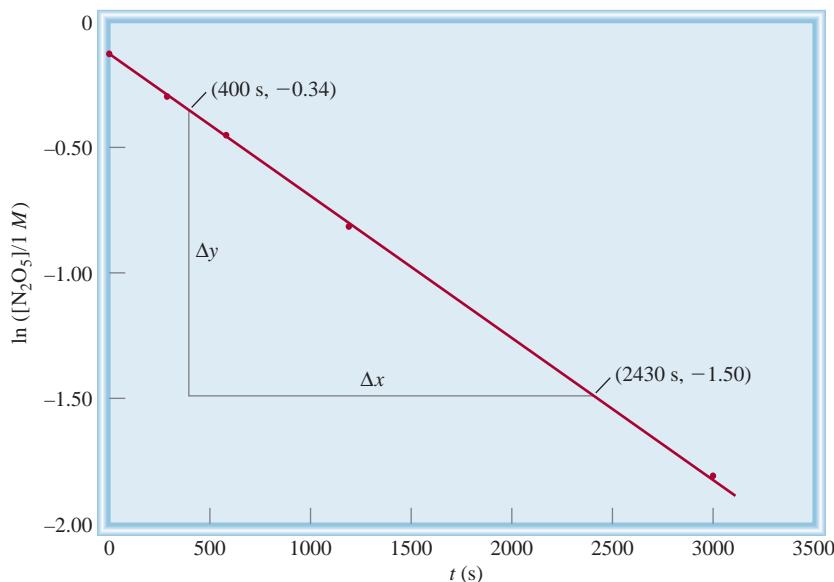


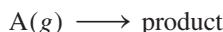
Figure 14.10 Decomposition of N_2O_5 . Plot of $\ln ([\text{N}_2\text{O}_5]/1 \text{ M})$ versus, time. The rate constant can be determined from the slope of the straight line.

required. The simplest, but least accurate, way is to select two data points far apart on the line and subtract their y and x values as follows:

$$\begin{aligned}\text{slope} &= \frac{\Delta y}{\Delta x} = \frac{\Delta \ln ([\text{N}_2\text{O}_5]/1 \text{ M})}{\Delta t} \\ &= \frac{-1.83 - (-0.094)}{(3000 - 0) \text{ s}} \\ &= -5.79 \times 10^{-4} \text{ s}^{-1}\end{aligned}$$

Because $\text{slope} = -k$, we get $k = 5.79 \times 10^{-4} \text{ s}^{-1}$. A more accurate method is to use least-squares linear regression (see Appendix 1) to find the line that best fits all the data. This method is tedious by hand, but can be performed readily either using a spreadsheet program or a simple scientific calculator. Using the data provided, the best-fit line from least squares linear regression gives $5.76 \times 10^{-4} \text{ s}^{-1}$, which is slightly different than the preceding simple estimate.

For gas-phase reactions, we can replace the concentration terms in Equations 14.5 and 14.6 with the partial pressures of the gaseous reactant. Consider the first-order reaction



Using the ideal gas equation we write

$$P_{\text{A}}V = n_{\text{A}}RT$$

or

$$\frac{n_{\text{A}}}{V} = [\text{A}] = \frac{P_{\text{A}}}{RT}$$

Substituting $[\text{A}] = P/RT$ into Equation 14.5, we get

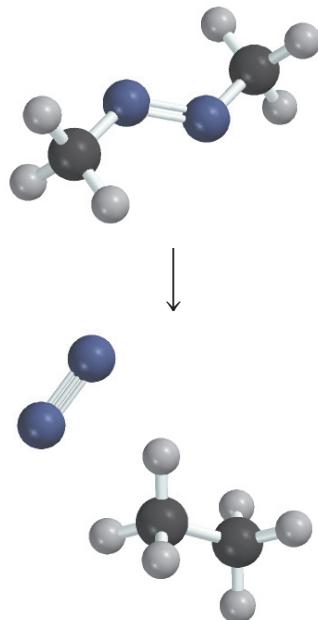
$$\ln \frac{[\text{A}]_t}{[\text{A}]_0} = \ln \frac{P_{\text{A},t}/RT}{P_{\text{A},0}/RT} = \ln \frac{P_{\text{A},t}}{P_{\text{A},0}} = -kt$$

The equation corresponding to Equation 14.7 now becomes

$$\ln \frac{P_{A,t}}{P_{\text{ref}}} = -kt + \ln \frac{P_{A,0}}{P_{\text{ref}}} \quad (14.8)$$

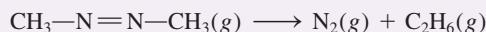
where P_{ref} is an arbitrary reference pressure (often 1 bar).

Example 14.4 shows the use of pressure measurements to study the kinetics of a first-order reaction.



Example 14.4

The rate of decomposition of azomethane is studied by monitoring the partial pressure of the reactant as a function of time:



The data obtained at 300°C are as follows:

| t (s) | P_{azo} (mmHg) | $\ln(P_{\text{azo}}/1 \text{ mmHg})$ |
|---------|-------------------------|--------------------------------------|
| 0 | 284 | 5.649 |
| 100 | 220 | 5.394 |
| 150 | 193 | 5.263 |
| 200 | 170 | 5.136 |
| 250 | 150 | 5.011 |
| 300 | 132 | 4.883 |

Are these values consistent with first-order kinetics? If so, determine the rate constant.

Strategy To test for first-order kinetics, determine whether the integrated first-order rate law (Equation 14.8 for pressure data) gives a straight line with the data provided. In this problem, pressure is measured in units of mmHg, so it is appropriate to use 1 mmHg as the reference pressure, P_{ref} . If the reaction is first order, then a plot of $\ln[P_{\text{azo}}(t)/(1 \text{ mmHg})]$ versus t will produce a straight line with a slope equal to $-k$.

Solution Figure 14.11, which is based on the data given in the table, shows that a plot of $\ln[P_{\text{azo}}(t)/(1 \text{ mmHg})]$ versus t yields a straight line, so the reaction is indeed first order. The slope of the line can be found by least-squares linear regression (see Appendix 1) and is equal to $2.55 \times 10^{-3} \text{ s}^{-1}$. According to Equation 14.8, the slope is equal to k , so $k = 2.55 \times 10^{-3} \text{ s}^{-1}$.

Practice Exercise Ethyl iodide ($\text{C}_2\text{H}_5\text{I}$) decomposes at a certain temperature in the gas phase as follows:



From the following data, determine the order of the reaction and the rate constant.

| t (min) | P_{azo} (bar) |
|-----------|------------------------|
| 0 | 0.36 |
| 15 | 0.30 |
| 30 | 0.25 |
| 48 | 0.19 |
| 75 | 0.13 |

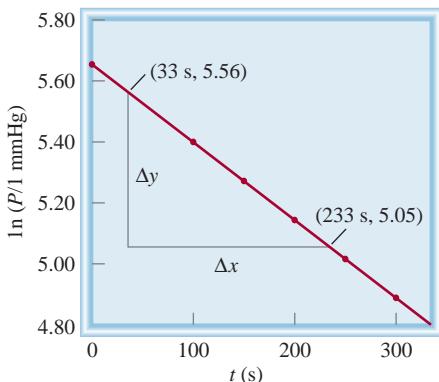


Figure 14.11 Plot of $\ln[P_{\text{azo}}(t)/(1 \text{ mmHg})]$ versus time for the decomposition of azomethane.

The Half-Life of a Reaction

A measure of considerable practical importance in kinetic studies is the **half-life** ($t_{1/2}$) of a reaction, which is *the time required for the concentration of a reactant to decrease to one-half of its initial concentration*. We can obtain an expression for $t_{1/2}$ for a first-order reaction as follows. At $t_{1/2}$, the concentration of reactant $[A]_t$ is equal to $[A]_0/2$, so Equation 14.5 becomes

$$\begin{aligned}\ln \frac{[A]_0/2}{[A]_0} &= -kt_{1/2} \\ \ln (1/2) &= -kt_{1/2} \\ -\ln(2) &= -kt_{1/2}\end{aligned}$$

so

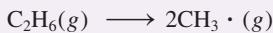
$$t_{1/2} = \frac{\ln(2)}{k} \approx \frac{0.693}{k} \quad (14.9)$$

The significance of Equation 14.9 is that the half-life of a first-order reaction is *independent* of the initial concentration of the reactant. Thus, it takes the same time for the concentration of the reactant to decrease from 1.0 M to 0.50 M , say, as it does for the concentration to decrease from 0.10 M to 0.050 M (Figure 14.12). Measuring the half-life of a reaction is one way to determine the rate constant of a first-order reaction. The shorter the half-life, the larger the k .

Example 14.5 shows how to calculate the half-life of a first-order reaction.

Example 14.5

The decomposition of ethane (C_2H_6) to methyl radicals is a first-order reaction with a rate constant of $5.36 \times 10^{-4} \text{ s}^{-1}$ at 700°C :



Calculate the half-life of the reaction in minutes.

Strategy Using Equation 14.9, calculate the half-life of a first-order reaction. The rate constant is given in units of s^{-1} , so a conversion of units is needed to express the half-life in minutes.

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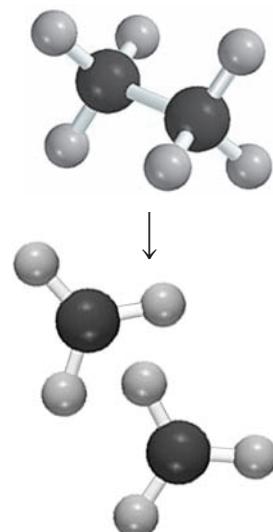
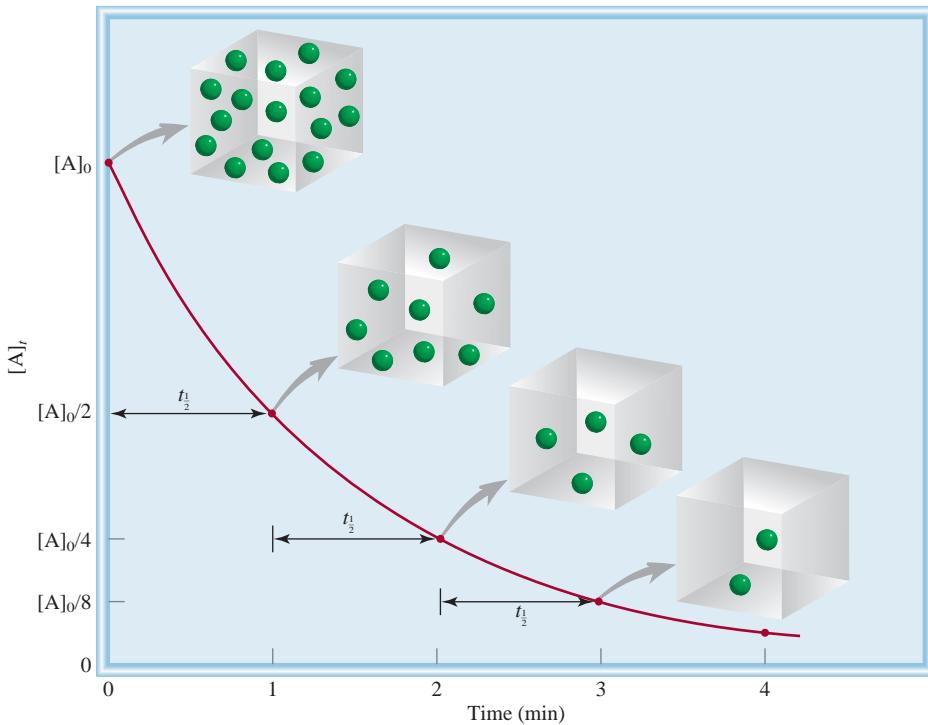


Figure 14.12 Plot of $[A]_t$ versus time for the first-order reaction $A \rightarrow \text{products}$. The half-life of the reaction is 1 min. After the elapse of each half-life, the concentration of A is halved.



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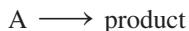
Solution For a first-order reaction, we only need the rate constant to calculate the half-life of the reaction. From Equation 14.9,

$$\begin{aligned} t_{1/2} &= \frac{\ln(2)}{k} \approx \frac{0.693}{k} = \frac{0.693}{5.36 \times 10^{-4} \text{ s}^{-1}} \\ &= 1.29 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \\ &= 21.5 \text{ min} \end{aligned}$$

Practice Exercise Calculate the half-life of the decomposition of N_2O_5 , discussed on page 726.

Second-Order Reactions

A **second-order reaction** is one whose rate depends on the concentration of one reactant raised to the second power or on the concentrations of two different reactants, each raised to the first power. The simplest type involves only one kind of reactant molecule:



From the rate law,

$$\text{rate} = -\frac{d[\text{A}]}{dt} = k[\text{A}]^2 \quad (14.10)$$

The units on k are $M^{-1} s^{-1}$. We can determine the dependence of $[A]$ on time by rearranging Equation 14.10 and integrating from the initial time ($t = 0$) and initial concentration ($[A]_0$) to the final time t and final concentration ($[A]_t$):

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = - \int_0^t k dt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

Rearranging gives the following integrated rate law for this second-order reaction:

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \quad (14.11)$$

We can obtain an equation for the half-life of a second-order reaction by setting $[A]_t = [A]_0/2$ in Equation 14.11.

$$\frac{1}{[A]_0/2} = kt + \frac{1}{[A]_0}$$

Solving for $t_{1/2}$ we obtain

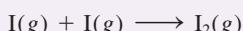
$$t_{1/2} = \frac{1}{k[A]_0} \quad (14.12)$$

The half-life of a second-order reaction is inversely proportional to the initial reactant concentration. This result makes sense because the half-life should be shorter in the early stage of the reaction when more reactant molecules are present to collide (react) with each other. Because of its dependence on concentration, the half-life is much less useful in describing second-order reactions than first-order reactions. Measuring the half-lives at different initial concentrations is one way to distinguish between a first-order and a second-order reaction.

The kinetic analysis of a second-order reaction is shown in Example 14.6.

Example 14.6

Iodine atoms combine to form molecular iodine in the gas phase:

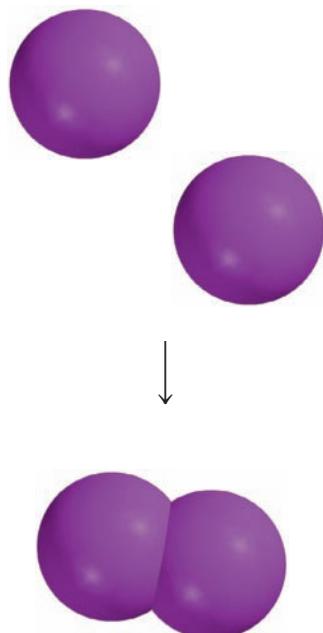


This reaction follows second-order kinetics with $k = 7.0 \times 10^9 M^{-1} s^{-1}$ at 23°C .

- (a) If the initial concentration of I was 0.086 M , calculate the concentration after 2.0 min. (b) Calculate the half-life of the reaction if the initial concentration of I is 0.60 M and if it is 0.42 M .

Strategy (a) The relationship between the concentrations of a reactant at different times is given by the integrated rate law. Because this is a second-order reaction with a single reactant, we must use Equation 14.11. (b) The half-life for a second-order reaction is given by Equation 14.12.

—Continued



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Solution (a) Given the initial concentration of I and the rate constant for the reaction, we can use Equation 14.11 to calculate the concentration of I at a later time:

$$\begin{aligned}\frac{1}{[I]_t} &= kt + \frac{1}{[I]_0} \\ \frac{1}{[I]_t} &= (7.0 \times 10^9 M^{-1} s^{-1}) \left(2.0 \text{ min} \times \frac{60 \text{ s}}{\text{min}} \right) + \frac{1}{0.086 M}\end{aligned}$$

where $[I]_t$ is the concentration at $t = 2.0 \text{ min}$. Solving the equation, we get

$$[I]_t = 1.2 \times 10^{-12} M$$

This is such a low concentration that it is virtually undetectable. The very large rate constant for the reaction means that practically all the I atoms have combined only 2.0 min into the reaction.

(b) We need Equation 14.12 to calculate the half-life of the reaction.

For $[I]_0 = 0.60 M$,

$$t_{1/2} = \frac{1}{k[I]_0} = \frac{1}{(7.0 \times 10^9 M^{-1} s^{-1})(0.60 M)} = 2.4 \times 10^{-10} \text{ s}$$

For $[I]_0 = 0.42 M$,

$$t_{1/2} = \frac{1}{k[I]_0} = \frac{1}{(7.0 \times 10^9 M^{-1} s^{-1})(0.42 M)} = 3.4 \times 10^{-10} \text{ s}$$

Comment These results confirm that the half-life of a second-order reaction, unlike that of a first-order reaction, is not a constant. Instead, the half-life of a second-order reaction depends on the initial concentration of the reactant(s).

Practice Exercise The reaction $2A \longrightarrow B$ is second order with a rate constant of $51 M^{-1} \text{ min}^{-1}$ at 24°C . (a) Starting with $[A]_0 = 0.0092 M$, how long will it take to reach $[A]_t = 3.7 \times 10^{-3} M$? (b) Calculate the half-life of the reaction.

The second-order integrated rate law derived above (Equation 14.11) applies to a reaction that is second-order in a single species. One can also have reactions such as



that is second order overall, but first order in each of the reacting species (A and B). The second-order rate law for this reaction is

$$\text{rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B] \quad (14.13)$$

This rate law can be integrated assuming $[A]_0 < [B]_0$ (Problem 14.92) to give an equation that relates the concentration of [A] and [B] to the initial concentrations and the elapsed time:

$$\frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0[B]}{[B]_0[A]} = kt \quad (14.14)$$

Equation 14.14 assumes that the stoichiometric coefficients for A and B are both unity. For other reactions, such as $A + 2B \longrightarrow$ products or $2A + B \longrightarrow$ products, the integrated second-order rate laws will be different, but can be derived in a similar manner.

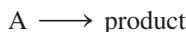
Equation 14.14 becomes greatly simplified if one of the reactants is present in large excess. For example, if $[A]_0 \gg [B]_0$, then the concentration of A will change very little as the reaction proceeds, that is, $[A]_t \approx [A]_0$. Substituting this into Equation 14.14 and using the approximation that $[B]_0 - [A]_0 \approx -[A]_0$, gives

$$\ln \frac{[B]}{[B]_0} = -k[A]_0 t$$

which is identical to a first-order integrated rate law in B (Equation 14.5) with a rate constant k^* equal to $k[A]_0$. Thus, due to one of the reactants being present in large excess, this mixed second-order reaction behaves approximates as a first-order reaction and is referred to as a **pseudo-first-order** reaction.

Zero-Order Reactions

First- and second-order reactions are the most common reaction types. Reactions whose order is zero are rare. For a zero-order reaction of the form



the rate law is given by

$$\text{rate} = k[A]^0 = k$$

Thus, the rate of a zero-order reaction is a *constant*, independent of reactant concentration. The integrated rate law for zero-order reactions is

$$[A]_t = [A]_0 - kt \quad (14.15)$$

with a half-life of $[A]_0/2k$. Third-order and higher order reactions are quite complex; they are not discussed in this book. Table 14.3 summarizes the kinetics for zero-order, first-order, and second-order reactions.

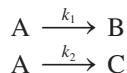
Table 14.3 Summary of the Kinetics of Zero-Order, First-Order, and Second-Order Reactions

| Order | Rate Law | Concentration-Time Equation | Half-Life |
|--|------------------|--|--|
| 0 | Rate = k | $[A]_t = -kt + [A]_0$ | $\frac{[A]_0}{2k}$ |
| 1 | Rate = $k[A]$ | $\ln \frac{[A]_t}{[A]_0} = -kt$ | $\frac{\ln(2)}{k} \approx \frac{0.693}{k}$ |
| 2 ($A \longrightarrow$ products) | Rate = $k[A]^2$ | $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$ | $\frac{1}{k[A]_0}$ |
| 2 ($A + B \longrightarrow$ products) | Rate = $k[A][B]$ | $\frac{1}{[B]_0 - [A]_0} \ln \frac{[A]_0[B]}{[B]_0[A]} = kt$ | — |

Other More Complex Reactions

Parallel Reactions

Consider a reactant that is involved in two first-order reactions that are occurring simultaneously (*parallel reactions*).



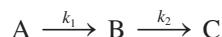
The total rate of consumption of A, is the sum of the rates for each of these reactions:

$$\frac{d[\text{A}]}{dt} = -k_1[\text{A}] - k_2[\text{A}] = -(k_1 + k_2)[\text{A}]$$

Thus, the rate of consumption of reactant A participating in simultaneous parallel reactions is governed by a rate constant that is the sum of the rate constants of the individual reactions.

Consecutive Reactions

A *consecutive reaction* is one in which the product from the first step becomes the reactant for the second step, and so on. To examine such reactions, consider the following two-step first-order consecutive reaction



Each step is first order, so the rate law equations for the concentrations for the disappearance of A and B are

$$\begin{aligned} \frac{d[\text{A}]}{dt} &= -k_1[\text{A}] \\ \frac{d[\text{B}]}{dt} &= k_1[\text{A}] - k_2[\text{B}] \end{aligned}$$

Assume that only A is present at time $t = 0$. Because the decrease in A is first order, Equation 14.6 holds. That is,

$$[\text{A}]_t = [\text{A}]_0 e^{-kt}$$

The integrated rate laws for B and C can be obtained using calculus:

$$[\text{B}] = \frac{k_1[\text{A}]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}); \quad [\text{C}] = [\text{A}]_0 \left[1 + \frac{1}{k_2 - k_1} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right] \quad (14.16)$$

Plots of the concentrations of A, B, and C for a reaction in which $k_1 = k_2$ are shown in Figure 14.13.

Consider the concentration of C in the limit that one reaction is much slower than the other. If the first reaction is the slowest ($k_1 \ll k_2$) then Equation 14.16 reduces to

$$[\text{C}] \approx [\text{A}]_0 (1 - e^{-k_1 t}) \quad k_1 \ll k_2$$

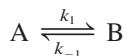
If the second reaction is the slowest ($k_2 \ll k_1$), then

$$[\text{C}] \approx [\text{A}]_0 (1 - e^{-k_2 t}) \quad k_2 \ll k_1$$

In both of these limits, it is the rate of the *slowest* reaction that determines the rate of formation of the product. This is a general feature of consecutive reactions. If one reaction step in a consecutive reaction is considerably slower than the other steps, then the rate constant of the slowest reaction will govern the rate of product formation. This slowest reaction is referred to as the **rate-determining step** in a reaction sequence. If $k_1 \ll k_2$, for the preceding reaction sequence, then the reaction $A \longrightarrow B$ is the rate-determining step. If, $k_2 \ll k_1$, on the other hand, then the reaction $B \longrightarrow C$ is rate determining.

Reversible Reactions

As we saw in Chapter 10, most reactions are, to some degree, reversible. To study the kinetics of a reversible reaction, it is necessary to take into account both the forward and the reverse rates. Consider, for example, a reversible first-order reaction of molecule A to form molecule B:



In this reaction, A is consumed in the forward reaction with rate constant k_1 and produced in the reverse reaction with a rate constant k_{-1} , so the net rate law is

$$\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$$

When the system reaches equilibrium, the concentration of A becomes constant in time, and the rate of production of A, given by $d[A]/dt$, will be equal to zero, giving

$$0 = -k_1[A] - k_{-1}[B]$$

Rearranging this equation gives

$$\frac{[B]}{[A]} = \frac{k_1}{k_{-1}} \quad (14.17)$$

The quantity on the left-hand side of Equation 14.17 ($[B]/[A]$) is the equilibrium constant K for the reaction $A \longrightarrow B$, so we have the result that the equilibrium constant is equal to the ratio of the forward and reverse reactions:

$$\frac{k_1}{k_{-1}} = K \quad (14.18)$$

The relationship between the rate constants of this reversible reaction and the equilibrium constant (Equation 14.18) is an example of the **principle of detailed balance**, which states that, at equilibrium, the rates of forward and reverse processes are equal.²

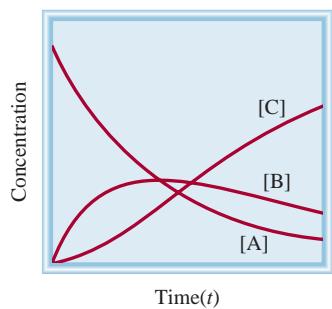


Figure 14.13 Variation in the concentrations of A, B, and C with time for the consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ for the case where $k_1 = k_2$.

2. The principle of detailed balance is a consequence of *microscopic reversibility*—the fact that the fundamental equations governing molecular motion (i.e., Newton's laws or the Schrödinger equation) have the same form when time t is replaced with $-t$ and the sign of all velocities (or momenta) are also reversed.

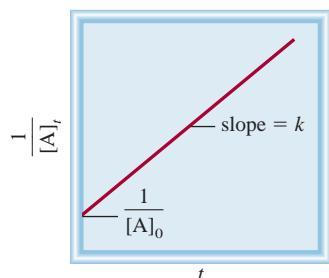


Figure 14.14 Typical dependence of the rate constant on temperature. The rate constants of most reactions increase with increasing temperature.

14.4 | The Arrhenius Equation Gives the Temperature Dependence of Rate Constants

With very few exceptions, reaction rates increase with increasing temperature. For example, the time required to hard-boil an egg in water is much shorter if the “reaction” is carried out at 100°C (about 10 min) than at 80°C (about 30 min). Conversely, an effective way to preserve foods is to store them at subzero temperatures, thereby slowing the rate of bacterial decay. Figure 14.14 shows a typical example of the relationship between the rate constant of a reaction and temperature. In order to explain this behavior, we must ask how reactions get started in the first place.

The Arrhenius Equation

In the late 1880s, the Swedish chemist Svante Arrhenius discovered that the temperature dependence of many reactions could be described empirically by the following equation, known as the *Arrhenius equation*:

$$k = Ae^{-E_a/RT} \quad (14.19)$$

where E_a (usually given in kJ mol^{-1}) is called the *activation energy* of the reaction, R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature, and e is the base of the natural logarithm scale. The quantity A is called the *frequency factor* (or *preexponential factor*) and is related to the frequency of collisions between reactant molecules. It can often be treated as a constant for a given reacting system over a fairly wide temperature range. Because the exponential of a quantity is a dimensionless number, the units of the frequency factor A are the same as for k .

Equation 14.19 can be expressed in a more useful form by taking the natural logarithm of both sides

$$\ln k = \ln Ae^{-E_a/RT}$$

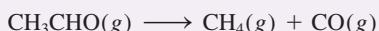
or

$$\ln k = \ln A - \frac{E_a}{RT} \quad (14.20)$$

In Equation 14.20, k and A are treated as dimensionless. This means that the values of k and A used in the equation represent the actual values of k or A divided by some reference value k_r . For example, if k is given as 1.2 s^{-1} , then we use 1 s^{-1} as k_r , and the value of k that we use in the equation is the dimensionless number 1.2. This will work as long as we use the same reference value for both k and A .

Example 14.7

The rate constants for the decomposition of acetaldehyde



were measured at five different temperatures, as shown in the accompanying table. Use these data to plot $\ln k$ versus $1/T$, and determine the activation energy

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Continued—

(in kJ mol^{-1}) for the reaction. (Note: The reaction is 3/2 order in CH_3CHO , so k has units of $M^{-1/2} \text{ s}^{-1}$.)

| $k (\text{M}^{-1/2} \text{ s}^{-1})$ | $T (\text{K})$ |
|--------------------------------------|----------------|
| 0.011 | 700 |
| 0.035 | 730 |
| 0.105 | 760 |
| 0.343 | 790 |
| 0.789 | 810 |

Strategy A plot of $\ln k$ versus $1/T$ will produce a straight line with a slope equal to $-E_a/R$. Thus, the activation energy can be determined from the slope of the plot.

Solution First, convert the data from k and T to $\ln k$ and $1/T$, respectively:

| $\ln k$ | $1/T (\text{K}^{-1})$ |
|---------|-----------------------|
| -4.51 | 1.43×10^{-3} |
| -3.35 | 1.37×10^{-3} |
| -2.254 | 1.32×10^{-3} |
| -1.070 | 1.27×10^{-3} |
| -0.237 | 1.23×10^{-3} |

A plot of these data yields the graph in Figure 14.14, which is linear. Using least-squares linear regression (see Appendix 1), the slope of the line that best fits these data is

$$\text{slope} = -2.09 \times 10^4 \text{ K}$$

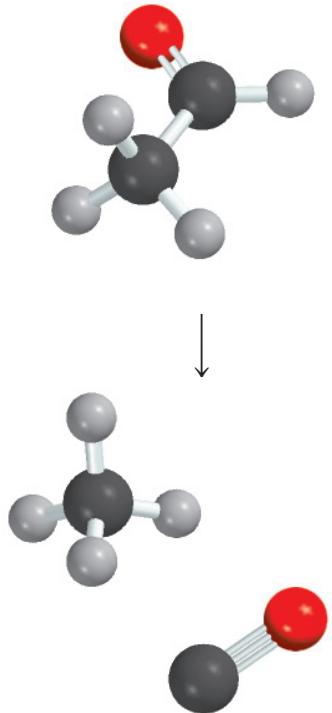
According to Equation 14.20, the slope is $-E_a/R$, so

$$\begin{aligned} -E_a/R &= \text{slope} = -2.09 \times 10^4 \text{ K} \\ E_a &= -(-2.09 \times 10^4 \text{ K})(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= 1.74 \times 10^5 \text{ J mol}^{-1} \\ &= 1.74 \times 10^2 \text{ kJ mol}^{-1} \end{aligned}$$

Practice Exercise The second-order rate constant for the decomposition of nitrous oxide (N_2O) into molecular nitrogen and an oxygen atom has been measured at different temperatures:

| $k (\text{M}^{-1} \text{ s}^{-1})$ | $T (\text{°C})$ |
|------------------------------------|-----------------|
| 1.87×10^{-3} | 600 |
| 0.0113 | 650 |
| 0.0569 | 700 |
| 0.244 | 750 |

Determine graphically the activation energy for the reaction.



If the frequency factor A is treated as if it were independent of temperature, an equation relating the rate constants k_1 and k_2 at temperatures T_1 and T_2 , respectively, can be used to calculate the activation energy or to find the rate constant at another temperature if the activation energy is known. To derive such an equation, we start with Equation 14.20:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

Subtracting $\ln k_2$ from $\ln k_1$ gives

$$\begin{aligned}\ln k_2 - \ln k_1 &= \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ \ln \frac{k_2}{k_1} &= \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ \ln \frac{k_2}{k_1} &= \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)\end{aligned}\tag{14.21}$$

Example 14.8 shows how to use Equation 14.21.

Example 14.8

The rate constant of a first-order reaction is $3.46 \times 10^{-2} \text{ s}^{-1}$ at 298 K. What is the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ mol^{-1} ?

Strategy Use Equation 14.21, a modified form of the Arrhenius equation, to relate two rate constants at two different temperatures. Make sure the units of R and E_a are consistent.

Solution The data are

$$\begin{array}{ll} k_1 = 3.46 \times 10^{-2} \text{ s}^{-1} & k_2 = ? \\ T_1 = 298 \text{ K} & T_2 = 350 \text{ K} \end{array}$$

Substituting the given temperatures and E_a into Equation 14.21 gives

$$\begin{aligned}\ln \frac{k_2}{k_1} &= \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \\ &= \frac{50.2 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left[\frac{350 \text{ K} - 298 \text{ K}}{(298 \text{ K})(350 \text{ K})} \right] \\ &= 3.01\end{aligned}$$

(We had to convert E_a to units of J mol^{-1} to match the units of R .) Exponentiating gives

$$\begin{aligned}\frac{k_2}{k_1} &= e^{3.01} = 20.3 \\ k_2 &= 20.3 \times k_1 = 20.3 \times 3.46 \times 10^{-2} \text{ s}^{-1} \\ &= 0.702 \text{ s}^{-1}\end{aligned}$$

—Continued

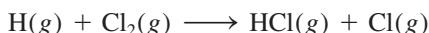
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Check The answer is reasonable because the rate constant is greater at a higher temperature.

Practice Exercise The first-order rate constant for the reaction of methyl chloride (CH_3Cl) with water to produce methanol (CH_3OH) and hydrochloric acid (HCl) is $3.32 \times 10^{-10} \text{ s}^{-1}$ at 25°C . Calculate the rate constant at 40°C if the activation energy is 116 kJ mol^{-1} .

Physical Meaning of the Activation Energy

In the course of a chemical reaction, chemical bonds in the reactants are broken and chemical bonds in the product are formed. The specific sequence in which these events occur is called the *reaction pathway*. Consider, for example, the simple gas-phase reaction of a hydrogen atom with molecular chlorine to form HCl and a Cl atom:



This reaction involves the breaking of a Cl—Cl bond and the formation of an H—Cl bond. To simplify the analysis, let us assume that the reaction occurs through the end-on collision of an H atom with the Cl_2 molecule as illustrated in Figure 14.15(a). When the hydrogen atom is well separated from the Cl_2 molecule, the system is in the initial reactant state [see Figure 14.15(a)] with a potential energy that is the sum of the potential energies for H and for Cl_2 [Figure 14.15(b)].

As the hydrogen atom nears the Cl—Cl molecule from the end [State 2 in Figure 14.15(b)], the electron clouds on both the H atom and the Cl_2 molecule will begin to distort and overlap, leading to the formation of a partial H—Cl bond and to a corresponding weakening of the Cl—Cl bond. Because we are replacing a full Cl—Cl bond with partial bonds, the potential energy of this intermediate state is higher than that of the initial reactant state as is shown in Figure 14.15(b). As the reaction proceeds, the potential energy continues to increase until it reaches a maximum at State 3, in which the central Cl atom is partially bonded to both the H and the other Cl. This *intermediate state, along the reaction pathway, at which the potential energy is a maximum*, is called the **transition state** (or **activated complex**). Continuing the reaction beyond the transition state, the potential energy decreases as the H—Cl bond strengthens with further weakening of the Cl—Cl bond (State 4), until the final product state (State 5) consisting of a fully formed H—Cl bond and a separated Cl atom is reached, and the potential energy is the sum of that for the separated products.

Because the bond enthalpy of the H—Cl bond (432 kJ mol^{-1}) is higher than that of the Cl—Cl bond (243 kJ mol^{-1}), energy is released in this reaction, so the potential energy of the product state is lower than that of the reactant state [$\Delta H = (243 - 432) \text{ kJ mol}^{-1} = -189 \text{ kJ mol}^{-1}$]. However, even though the net reaction goes downhill in energy, the reaction can only proceed if the kinetic energy of the collision is sufficient to enable the system to reach the transition state—otherwise the H atom will simply rebound from the collision with no reaction occurring. The difference in potential energy between the transition state and the initial reactant state is precisely the *activation energy* (E_a) that appears in the Arrhenius equation (Equation 14.19), and represents the *minimum amount of energy required for a chemical reaction to proceed*.

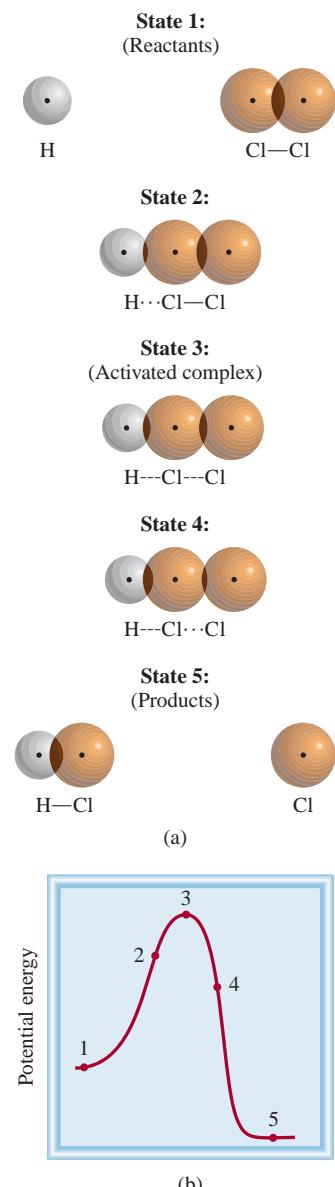


Figure 14.15 (a) Stages of the gas-phase reaction of the end-on reaction of atomic hydrogen with molecular chlorine: $\text{H}(g) + \text{Cl}_2(g) \longrightarrow \text{HCl}(g) + \text{Cl}(g)$. (b) The potential energy profile of the reaction showing each of the stages in part (a).

Figure 14.16 Potential energy profiles for (a) exothermic and (b) endothermic reactions. These plots show the change in potential energy as reactants A and B are converted to products C and D. The transition state (AB^{\ddagger}) is a highly unstable species with a high potential energy. The activation energy is defined for the forward reaction in both (a) and (b). The products C and D are more stable than the reactants in (a) and less stable than the reactants in (b).

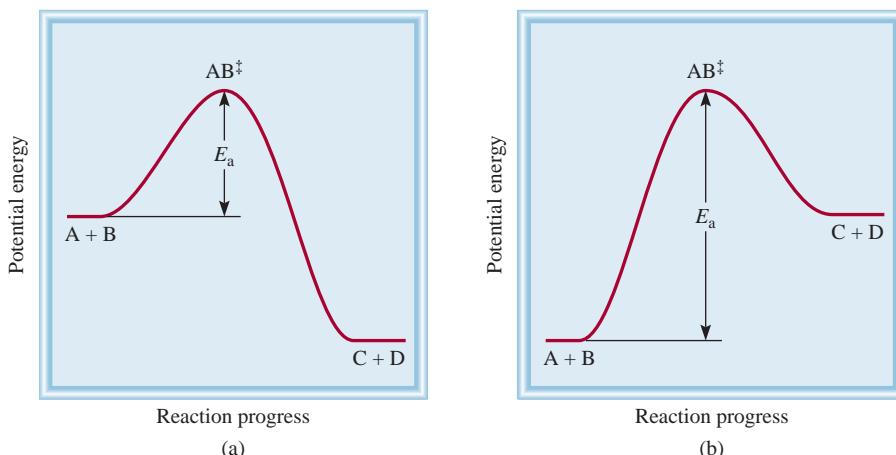
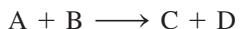
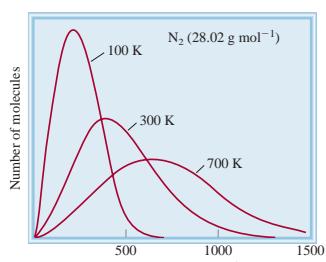


Figure 14.16 shows two different potential energy profiles for the generic reaction



If the products are more stable than the reactants, then the reaction will release heat, that is, the reaction will be exothermic [Figure 14.16(a)]. If the products are less stable than the reactants, on the other hand, then the reaction will absorb heat from the surroundings, and we have an endothermic reaction [Figure 14.16(b)]. In both cases, we plot the potential energy of the reacting system versus the progress of the reaction, with the transition state denoted by AB^{\ddagger} . Qualitatively, these graphs show how potential energy changes as reactants are converted to products.

We can think of activation energy as a barrier that prevents less energetic molecules from reacting. Because the number of reactant molecules in an ordinary reaction is very large, the speeds, and hence the kinetic energies of the molecules, vary greatly. Normally, only a small fraction of the colliding molecules—the fastest-moving ones—have enough kinetic energy to exceed the activation energy. These molecules can therefore take part in the reaction. The increase in the rate (or the rate constant) with temperature according to Equation 14.19 can now be explained: The speeds of the molecules obey the Maxwell-Boltzmann distributions shown in Figure 5.19(a) (reproduced in margin). If we compare the speed distributions at two different temperatures, we see that more high-energy molecules are present at the higher temperature. The rate of product formation is, therefore, also greater at the higher temperature.



The Maxwell-Boltzmann distribution of molecular speeds for N_2 at three different temperatures.

The Collision Theory of Reaction Rates

For reactions taking place in the gas phase, both the Arrhenius equation and the dependence of the rate law on concentration can be accounted for using the kinetic theory of gases, giving what we call the *collision theory* of gas-phase chemical kinetics. In this theory, the rate of a reaction is directly proportional to the number of molecular collisions per second (i.e., to the frequency of molecular collisions):

$$\text{rate} \propto \frac{\text{number of collisions}}{\text{s}}$$

Consider the following gas-phase reaction involving the collision of two B molecules to form products:



Using the kinetic theory of gases (Chapter 5), the number of two-particle collisions (Z_{BB}) that take place per volume (V) per unit time can be determined to be

$$Z_{\text{BB}} = \frac{\sqrt{2}}{2} \pi d^2 \langle u \rangle \left(\frac{N_{\text{B}}}{V} \right)^2 \quad (14.22)$$

where d is the diameter of molecule B (assumed to be a hard sphere), N_{B} is the number of B molecules, and $\langle u \rangle$ is the mean molecular speed. The mean molecular speed was given in Equation 5.42 as

$$\langle u \rangle = \sqrt{\frac{8k_{\text{B}}T}{\pi m}}$$

where m is the mass of molecule B, k_{B} is Boltzmann's constant, and T is the absolute temperature. Combining Equation 5.42 with the relation that $N_{\text{B}}/V = N_{\text{A}}[\text{B}]$, where N_{A} is Avogadro's number, gives

$$Z_{\text{BB}} = \left[2d^2 N_{\text{A}}^2 \sqrt{\frac{\pi k_{\text{B}} T}{m}} \right] [\text{B}]^2 \quad (14.23)$$

Now, if every collision produced a reaction, the rate of this reaction would equal Z_{BB} . However, generally only a small fraction of the collisions will be sufficiently energetic to overcome the activation barrier. As a result, the collision frequency in Equation 14.23 must be multiplied by the fraction of the collisions that have kinetic energies larger than E_{a} . Using the Maxwell-Boltzmann distribution of molecular speeds (Equation 5.38), it can be shown that the collision frequency must be multiplied by a factor $e^{-E_{\text{a}}/RT}$ to account for the fact that not all collisions will be of sufficient energy to react. The rate then becomes

$$\text{rate} = Z_{\text{BB}} e^{-E_{\text{a}}/RT} = \left[2d^2 N_{\text{A}}^2 \sqrt{\frac{\pi k_{\text{B}} T}{m}} \right] e^{-E_{\text{a}}/RT} [\text{B}]^2 \quad (14.24)$$

This rate expression correctly identifies both the concentration dependence of the rate law (second order in B) and the temperature dependence of the rate constant, which from Equation 14.24 is

$$k = \left[2d^2 N_{\text{A}}^2 \sqrt{\frac{\pi k_{\text{B}} T}{m}} \right] e^{-E_{\text{a}}/RT} \quad (14.25)$$

Comparing Equation 14.25 with the Arrhenius equation (Equation 14.19), we get

$$A = \left[2d^2 N_{\text{A}}^2 \sqrt{\frac{\pi k_{\text{B}} T}{m}} \right] \quad (14.26)$$

Thus, the frequency factor, A , predicted by the collision theory of chemical kinetics is temperature dependent. In practice, we can usually treat it as a temperature-independent quantity in the calculation of E_{a} values. Doing so does not introduce any serious error because the exponential term ($e^{-E_{\text{a}}/RT}$) depends so much more strongly on temperature than the square-root term in A (Equation 14.26).

For a bimolecular reaction of the type



the collision frequency is similar, except that the mass m is replaced by the reduced mass, μ , of the B and C pair

$$\mu = \frac{m_{\text{B}}m_{\text{C}}}{m_{\text{B}} + m_{\text{C}}}$$

and the diameter d is replaced by the mean diameter $d_{\text{BC}} = (d_{\text{B}} + d_{\text{C}})/2$. With these changes, the collision theory expression for the rate of this bimolecular reaction is

$$\text{rate} = Z_{\text{BC}}e^{-E_a/RT} = \left[d_{\text{BC}}^2 N_{\text{A}}^2 \sqrt{\frac{\pi k_{\text{B}} T}{\mu}} \right] e^{-E_a/RT} [\text{B}][\text{C}] \quad (14.27)$$

and

$$k = \left[d_{\text{BC}}^2 N_{\text{A}}^2 \sqrt{\frac{\pi k_{\text{B}} T}{\mu}} \right] e^{-E_a/RT} \quad (14.28)$$

which correctly predicts that the rate is first order in B, first order in C, and second order overall.

The collision theory expressions for the rate constants (Equations 14.25 and 14.28) do a good job of predicting rate constants for reactions that involve atomic species or simple radicals, given the activation energy. However, for more complex reactants, collision theory tends to overestimate the rate constants, often by a large factor. This discrepancy arises because our simple collision theory assumes that a reaction will occur if the collision has a kinetic energy that is sufficient to overcome the activation barrier. However, even if the collision is sufficiently energetic, a reaction may not occur because the reacting molecules are not oriented optimally relative to one another. This effect can be accounted for by modifying Equation 14.28 (or 14.25) to include an ***orientation factor*** (or ***steric factor***) P :

$$k = P Z e^{-E_a/RT} \quad (14.29)$$

The factor P , which is often quite difficult to calculate, represents the fraction of colliding molecules that are properly oriented for reaction to occur.

As an example, consider the gas-phase reaction between potassium (K) atoms and methyl iodide (CH_3I) to form potassium iodide (KI) and a methyl radical ($\text{CH}_3\cdot$):



This reaction is most favorable when the K atom collides with the I atom in CH_3I head-on (Figure 14.17). Otherwise, few or no products are formed.

Transition-State Theory

Collision state theory is useful for gas-phase reactions of simple atoms and molecules, but it cannot adequately predict reaction rates for more complex molecules or molecules in solution. Another approach, called ***transition-state theory*** (or ***activated-complex theory***), was developed by Henry Eyring and others in the 1930s. Because it is applicable to a wide range of reactions, transition-state theory has become the major theoretical tool in the prediction of chemical kinetics.

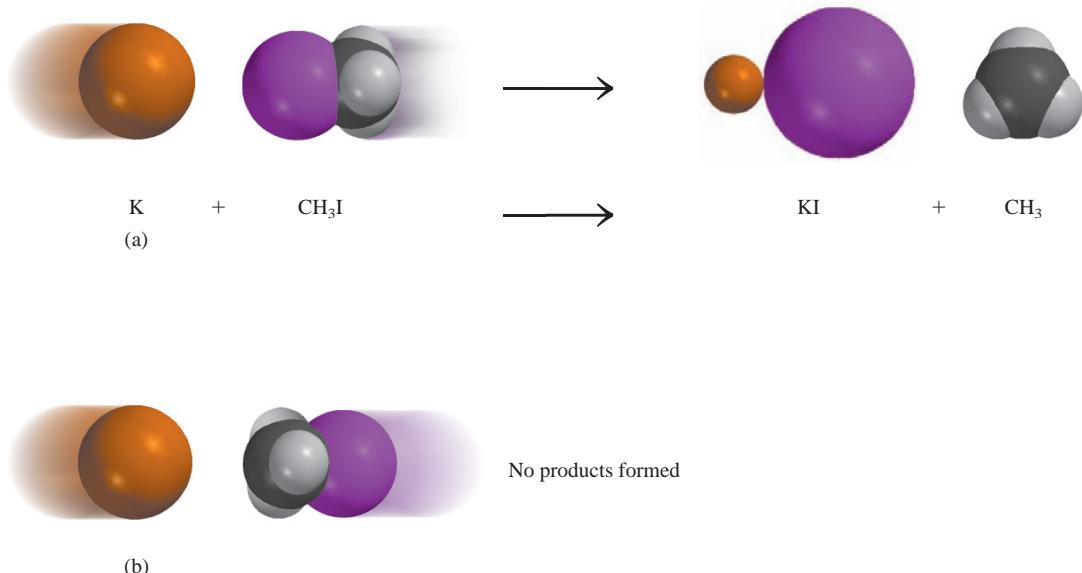


Figure 14.17 Relative orientation of reacting molecules. Only when the K atoms collides with the I atom head-on will the reaction most likely occur.

Consider a reaction between A and B that proceeds to products through a transition state labeled AB^{\ddagger} , as shown in Figure 13.6. The central assumption of transition-state theory is that, as the reaction proceeds, the reactants A and B are in equilibrium with the transition state AB^{\ddagger} , that is, we assume that the forward and backwards rate constants between A + B and AB^{\ddagger} are much faster than the rate constant for the decomposition of the AB^{\ddagger} :



The concentration equilibrium constant, K_c^{\ddagger} , between the reactants and the transition state can be written as

$$K_c^{\ddagger} = \frac{[\text{AB}^{\ddagger}]}{[\text{A}][\text{B}]} \quad (14.30)$$

In terms of this equilibrium constant, it can be shown using statistical mechanics that the transition-state theory estimate for the rate constant is given by

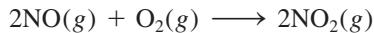
$$k = \frac{k_B T}{h} K_c^{\ddagger} c_0^{1-m} \quad (14.31)$$

where h is Planck's constant, k_B is Boltzmann's constant, T is the absolute temperature, m is the reaction order, and c_0 is the standard concentration (1.0 M). The factor of c_0^{1-m} is necessary to ensure that k has the appropriate units. The equilibrium constant K_c^{\ddagger} can be calculated using standard computational chemistry software, or from physical properties of the reactants (bond lengths, bond angles and vibrational frequencies) of the reactants.

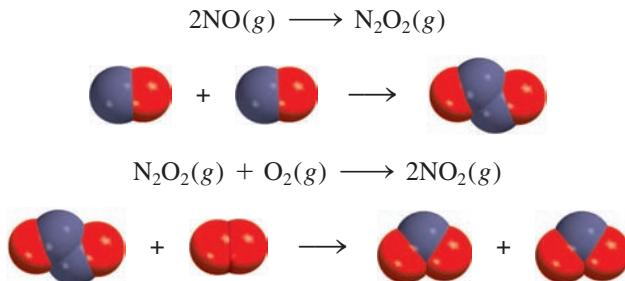
14.5 | The Reaction Mechanism Is the Sequence of Elementary Steps That Lead to Product Formation

An overall balanced chemical equation does not tell us much about how a reaction actually takes place. In many cases, it merely represents the sum of several **elementary steps** (or *elementary reactions*), *a series of simple reactions that represent the progress of the overall reaction at the molecular level*. The *sequence of elementary steps that leads to product formation* is called the **reaction mechanism**. The reaction mechanism is comparable to the route traveled during a trip; the overall chemical equation specifies only the origin and final destination. The details of the reaction mechanism (or pathway) connecting given initial and final states have profound effects on the rate of a reaction. This is in contrast to the situation in chemical thermodynamics, where we saw that the changes in thermodynamic state functions were independent of the path taken between initial and final states. The reaction mechanism cannot be deduced from the stoichiometry of the overall reaction but must be postulated based on experimental evidence.

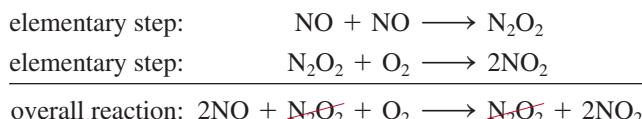
To better understand the reaction mechanism, consider the reaction between nitric oxide and oxygen:



We know from experiment that the products are not formed directly from the collision of two NO molecules with an O₂ molecule because N₂O₂ is detected during the course of the reaction. Let us assume that the reaction actually takes place via two elementary steps as follows:



In the first elementary step, two NO molecules collide to form an N₂O₂ molecule. This event is followed by the reaction between N₂O₂ and O₂ to give two molecules of NO₂. The net chemical equation, which represents the overall change, is given by the sum of the elementary steps:



The sum of the elementary steps must give the overall reaction.

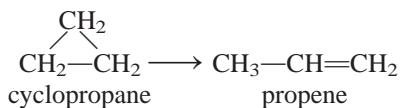
Species such as N₂O₂ are called **reaction intermediates** because they *appear in the mechanism of the reaction (i.e., in the elementary steps) but not in the overall balanced equation*. An intermediate is always formed in an early elementary step and consumed in a later elementary step.

The **molecularity of a reaction** is *the number of molecules reacting in an elementary step*. These molecules may be of the same or different types. Each of the elementary steps just discussed is **bimolecular** because each involves two molecules. **Unimolecular**

reactions, elementary steps in which only one reacting molecule participates, include the decomposition of N_2O_4 to form NO_2



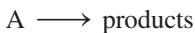
and the conversion of cyclopropane to propene,



Very few **termolecular reactions**, which are reactions that involve three molecules in one elementary step, are known, because the simultaneous encounter of three molecules in the proper orientation to react is a far less likely event than a bimolecular collision or a unimolecular reaction.

Rate Laws for Elementary Steps

Knowing the elementary steps of a reaction enables us to deduce the rate law. Suppose, for example, that we have the following elementary reaction:



Because there is only one molecule present, this is a unimolecular elementary reaction. It follows that the larger the number of A molecules present, the faster the rate of product formation. Thus, the rate of a unimolecular elementary reaction is directly proportional to the concentration of A (that is, it is first order in A):

$$\text{rate} = k[\text{A}]$$

For a bimolecular elementary reaction involving A and B molecules,



the rate of product formation depends on how frequently A and B collide, which in turn depends on the concentrations of A and B. Thus, we can express the rate as

$$\text{rate} = k[\text{A}][\text{B}]$$

Similarly, for a bimolecular elementary reaction of the type



the rate becomes

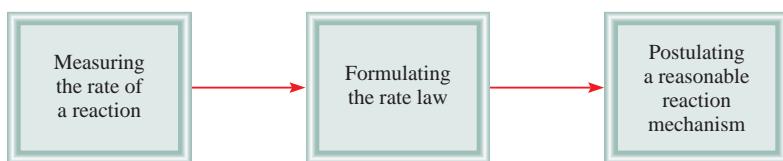
$$\text{rate} = k[\text{A}]^2$$

The preceding examples show that the reaction order for each elementary reactant is equal to its stoichiometric coefficient in the chemical equation for that step. In general, we cannot tell by merely looking at the overall balanced equation whether the reaction occurs as shown or in a series of steps. This determination is made in the laboratory.

Rate Laws and Reaction Mechanisms

Experimental studies of reaction mechanisms begin with the collection of data (rate measurements). Next, we analyze the data to determine the rate constant and order of the reaction, and we write the rate law. Finally, we suggest a plausible mechanism for

Figure 14.18 Sequence of steps in the study of a reaction mechanism.



the reaction consisting of elementary steps (Figure 14.18). The elementary steps must satisfy two requirements:

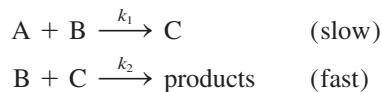
- ▶ The sum of the elementary steps must give the overall balanced equation for the reaction.
- ▶ The rate-determining step should predict a rate law that is identical to the one determined experimentally.

For a proposed reaction mechanism, we must be able to detect the presence of any intermediate(s) formed in one or more elementary steps.

To evaluate whether the second criterion is satisfied, we must be able to construct the rate law based on a candidate reaction mechanism. This is often a complex procedure that requires approximations. If one step is significantly slower than the others, however, then the determination of the rate law is considerably simplified. In Section 14.3, we saw that when a reaction occurs in a series of consecutive individual steps, the rate of the overall process is governed by the rate of the slowest, or rate-determining, step. Consider, for example, the reaction



The reaction is observed to be first order in both A and B and second order overall. Thus, the reaction cannot take place in a single elementary step corresponding to the overall reaction because then it would be second order in B, contrary to observation. Therefore, multiple elementary steps must be involved in the reaction mechanism. A proposed mechanism is



Because $k_1 \ll k_2$, the first bimolecular elementary step is rate determining, and the rate law can be written as

$$\text{rate} = -\frac{d[A]}{dt} = k_1[A][B]$$

which is consistent with the observed rate law. The potential energy profile for such a reaction is shown in Figure 14.19. The first step, which is rate determining, has a larger activation energy than the second step. The intermediate, although stable enough to be observed, reacts quickly to form the products.

Decomposition of Hydrogen Peroxide

An example of this type of reaction is the decomposition of hydrogen peroxide, which is facilitated by iodide ions (Figure 14.20). The overall reaction is

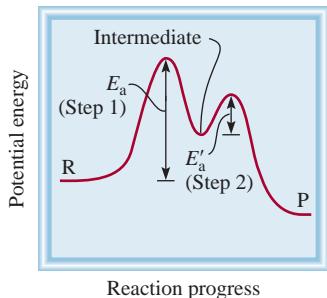
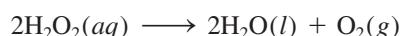


Figure 14.19 Potential energy profile for a two-step reaction in which the first step is rate determining. R and P represent reactants and products, respectively.



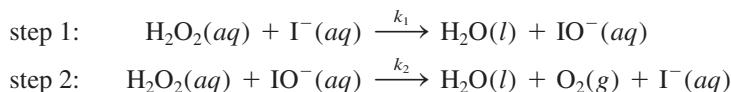
Figure 14.20 The decomposition of hydrogen peroxide is catalyzed by iodine ions. A few drops of liquid soap have been added to the solution to dramatize the evolution of oxygen gas. (Some of the iodide ions are oxidized to molecular iodine, which then reacts with iodide ions to form the brown triiodide ion I_3^- .)

Experimentally, the rate law is found to be

$$\text{rate} = k [\text{H}_2\text{O}_2][\text{I}^-]$$

Thus, the reaction is first order with respect to both H_2O_2 and I^- .

The H_2O_2 decomposition does not occur in a single elementary step corresponding to the overall balanced equation. If it did, the reaction would be second order in H_2O_2 (due to the collision of two H_2O_2 molecules). What's more, the I^- ion, which is not even part of the overall equation, appears in the rate law expression. How can we reconcile these facts? First, we can account for the observed rate law by assuming that the reaction takes place in two separate elementary steps, each of which is bimolecular:



If we further assume that step 1 is rate determining, then the rate of the reaction can be determined from the first step alone:

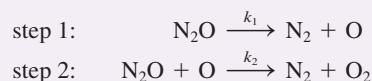
$$\text{rate} = k_1[\text{H}_2\text{O}_2][\text{I}^-]$$

where $k_1 \ll k_2$. The IO^- ion is an intermediate because it does not appear in the overall balanced equation. Although the I^- ion also does not appear in the overall equation, I^- differs from IO^- because I^- is present at the start of the reaction and at its completion. The function of I^- is to speed up the reaction, that is, it is a *catalyst*. We discuss catalysis in Section 14.6.

Example 14.9 concerns the mechanistic study of a relatively simple reaction.

Example 14.9

The gas-phase decomposition of nitrous oxide (N_2O) is believed to occur via two elementary steps:



Experimentally, the rate law is found to be $\text{rate} = k [\text{N}_2\text{O}]$. (a) Write the equation for the overall reaction. (b) Identify the intermediates. (c) What can you say about the relative rates of steps 1 and 2?

Strategy (a) Because the overall reaction can be broken down into elementary steps, knowing the elementary steps would enable us to write the overall reaction. (b) Reaction intermediates appear as the product of one elementary reaction and as a reactant of a subsequent elementary reaction, so intermediates do not appear in the overall chemical reaction. (c) Based on the experimental rate law, determine which of the steps is rate determining.

Solution (a) Adding the equations for steps 1 and 2 gives the following overall reaction:



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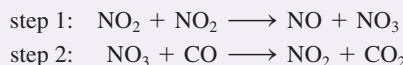
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- (b) Because the O atom is produced in the first elementary step, is consumed in the second elementary step, and does not appear in the overall balanced equation, it is an intermediate.
- (c) If we assume that step 1 is rate determining (that is, if $k_2 \gg k_1$), then the rate of the overall reaction is given by

$$\text{rate} = k_1[\text{N}_2\text{O}]$$

and $k = k_1$, which is consistent with the experimental rate law. If step 2 were rate determining, then the rate law would be second order, which is inconsistent with the experimental rate law, so we can conclude that step 1 is slow relative to step 2.

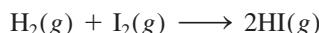
Practice Exercise The reaction between NO_2 and CO to produce NO and CO_2 is believed to occur via the following two steps:



The experimental rate law is $\text{rate} = k [\text{NO}_2]^2$. (a) Write the equation for the overall reaction. (b) Identify any reaction intermediate. (c) What can you say about the relative rates of steps 1 and 2?

The Formation of Hydrogen Iodide

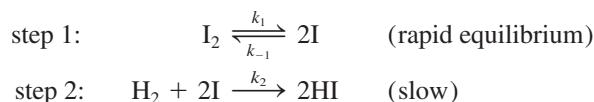
Another common reaction mechanism is one that has at least two elementary steps, the first of which is very rapid in both the forward and reverse directions compared with the second step. This kind of reaction mechanism has a **rapid preequilibrium**. An example is the reaction between molecular hydrogen and molecular iodine to produce hydrogen iodide:



Experimentally, the rate law is found to be

$$\text{rate} = k [\text{H}_2][\text{I}_2]$$

For many years, it was thought that the reaction occurred just as written, that is, the reaction consists of a bimolecular elementary step involving a hydrogen molecule and an iodine molecule. In the 1960s, however, chemists proposed a more complicated two-step mechanism:



where k_1 , k_{-1} , and k_2 are the rate constants for the reactions. The I atoms are intermediates in this reaction.

When the reaction begins, there are very few I atoms present. As I_2 dissociates, though, the concentration of I_2 decreases while that of I increases. Therefore, the forward rate of step 1 decreases and the reverse rate increases. Soon the two rates become equal, and a chemical equilibrium is established. Because the elementary reactions in step 1 are much faster than the one in step 2, equilibrium is reached

before any significant reaction with hydrogen occurs, and it persists throughout the reaction.

The rate of the reaction is given by the slow, rate-determining step, which is step 2—a termolecular reaction between H₂ and two I atoms:

$$\text{rate} = k_2[\text{H}_2][\text{I}]^2$$

This rate law is of limited usefulness because it contains the concentration of I, which is difficult to monitor because I is an intermediate. To eliminate the concentration of the intermediate from the rate law, we can use the principle of detailed balance (Section 14.3). According to this principle, the forward rate at equilibrium must equal the reverse rate, that is,

$$k_1[\text{I}_2] = k_{-1}[\text{I}]^2$$

or

$$[\text{I}]^2 = \frac{k_1}{k_{-1}} [\text{I}_2] = K [\text{I}_2]$$

where $K = k_1/k_{-1}$ is the equilibrium constant for step 1 (see Equation 14.18). Substituting this expression for [I]² into the rate law, we obtain

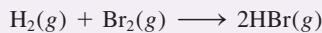
$$\begin{aligned}\text{rate} &= \frac{k_2 k_1}{k_{-1}} [\text{H}_2][\text{I}_2] = k_2 K [\text{H}_2][\text{I}_2] \\ &= k[\text{H}_2][\text{I}_2]\end{aligned}$$

where $k = k_1 k_2 / k_{-1} = k_2 K$. As you can see, this two-step mechanism also gives the correct rate law for the reaction. This agreement along with the experimental observation of intermediate I atoms provides evidence that the mechanism is correct. However, keep in mind that demonstrating that a particular reaction mechanism is consistent with the experimental rate law does not prove conclusively that the mechanism is correct, as there may be other, yet unknown, mechanisms that also give the correct rate law.

Example 14.10 examines another example of a reaction mechanism with a pre-equilibrium condition.

Example 14.10

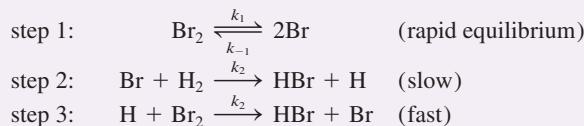
Under certain conditions, the experimental rate law for the gas-phase reaction of molecular hydrogen with molecular bromine



is given by

$$\text{rate} = k [\text{H}_2][\text{Br}_2]^{1/2}$$

Show that the unusual half-reaction order for Br₂ can be explained by the following mechanism:



—Continued

Continued—

Strategy The second step is rate determining, but its rate law contains the intermediate Br atom. To eliminate [Br] from the rate law, use the fact that the forward and back reactions in step 1 are in rapid equilibrium.

Solution Because the second step is slow and rate determining, the rate law is given by

$$\text{rate} = k_2[\text{Br}][\text{H}_2]$$

Because Br is an intermediate, it is necessary to eliminate it from the rate law. To do this we note that the first step is in rapid equilibrium, so we can assume that

$$K = \frac{k_1}{k_{-1}} = \frac{[\text{Br}]^2}{[\text{Br}_2]}$$

Solving for [Br] gives

$$[\text{Br}]^2 = \frac{k_1}{k_{-1}} [\text{Br}_2]$$

or

$$[\text{Br}] = \sqrt{\frac{k_1}{k_{-1}}} [\text{Br}_2]^{1/2}$$

Substituting this expression for the intermediate concentration [Br] into the rate law for the rate-determining step (step 2) gives

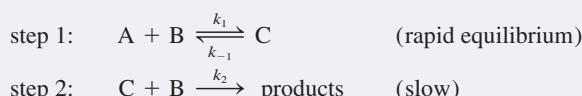
$$\begin{aligned}\text{rate} &= k_2[\text{Br}][\text{H}_2] = k_2 \sqrt{\frac{k_1}{k_{-1}}} [\text{Br}_2]^{1/2} [\text{H}_2] \\ &= k [\text{Br}_2]^{1/2} [\text{H}_2]\end{aligned}$$

where $k = k_2(k_1/k_{-1})^{1/2}$, which is consistent with the observed rate law.

Practice Exercise A reaction $\text{A} + 2\text{B} \longrightarrow$ products has the rate law

$$\text{rate} = k[\text{A}][\text{B}]^2$$

Show that this rate law is consistent with the following mechanism:

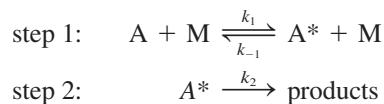


What is the rate constant k in terms of k_1 , k_{-1} , and k_2 ? Can you suggest an experiment that could distinguish between this proposed mechanism and a direct termolecular combination of one A molecule and two B molecules, which would have a rate that was also consistent with the experimental rate law?

The Steady-State Approximation

Not all reactions have a single rate-determining step. A reaction may have two or more comparably slow steps. The kinetic analysis of such reactions is generally more involved. One approximation that is useful in such cases is to assume that the concentration of intermediates is constant over much of the reaction progress. Consider,

for example, the following mechanism for the decomposition of A to products that was proposed by Frederick Lindemann³ in 1922 to explain the observed pressure dependence of the rate law for many unimolecular reactions:



In the first step, the molecule A collides with another molecule in the forward direction and is excited to a high energy state denoted as A*. The excited molecule (A*) can then collide with another molecule to become deexcited back to the low energy form (A) in the reverse of step 1, or, in the second step, it can fall apart to form the products.

From this mechanism the rate of formation of the products is

$$\text{rate} = k_2[A^*] \quad (14.32)$$

If we do not know the relative magnitudes of k_1 , k_{-1} , and k_2 , we cannot assume rapid preequilibrium to eliminate the concentration of the intermediate A* from the rate law. Instead, we assume that after an initial rise, the concentration of the intermediate A* becomes constant as the rates of activation, deactivation, and decomposition become balanced. Thus,

$$\text{rate of } A^* \text{ production} = \frac{d[A^*]}{dt} \approx 0$$

That is, the concentration of A* achieves a *steady state* during the reaction. From the reaction mechanism, the rate of A* production is given by the rate of activation in step 1 ($k_1[A][M]$) minus the rate of deactivation in step 1 ($k_{-1}[A^*][M]$) and minus the rate of decomposition ($k_2[A^*]$):

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*]$$

Setting the rate of production of A* to zero yields

$$k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*] \approx 0$$

which, after arrangement becomes

$$[A^*] = \frac{k_1[A][M]}{k_2 + k_{-1}[M]} \quad (14.33)$$

Equation 14.33 gives the ***steady-state approximation*** for the concentration of A*. Substituting this into the rate law (Equation 14.32) gives the ***steady-state rate law***

$$\text{rate} = \frac{k_1 k_2 [A][M]}{k_2 + k_{-1}[M]} \quad (14.34)$$

3. Frederick Alexander Lindemann (1886–1957). German/British physicist. Lindemann was born and educated in Germany, but spent most of his scientific and political career in England. He made numerous contributions to the thermodynamics of materials and to chemical reaction dynamics. While in the Royal Air Corps during World War I, he developed a mathematical theory of airplane rotation that enabled pilots to recover from uncontrolled spin. He was very active in British politics, serving as scientific advisor to Winston Churchill during World War II. Lindemann was instrumental in the creation of the United Kingdom Atomic Energy Agency.

As Equation 14.34 shows, rate laws derived from the steady-state approximation are generally more complicated than those in which one step can be assumed to be rate limiting. Let's examine the dependence of this rate law in two limits. For an ideal gas system, the concentration of molecules with which A can collide is directly proportional to the total pressure. When the system is at low pressure, there are relatively few molecules with which to collide and $[M]$ is small. In this limit, $k_2 \gg k_{-1}[M]$, and Equation 14.34 becomes

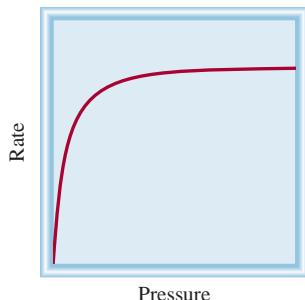


Figure 14.21 Plot of the pressure dependence of the rate for a unimolecular decomposition that follows the Lindemann mechanism

Thus, the rate is second order overall and shows a linear increase with total pressure. At high pressures, $[M]$ is large and $k_2 \ll k_{-1}[M]$, so Equation 14.34 becomes

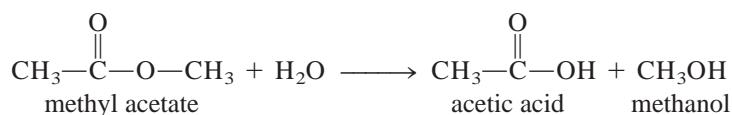
high pressure: rate = $\frac{k_1}{k_{-1}} [A]$

In this case, the rate law is first order in A and independent of the total pressure. A plot of the pressure dependence of a unimolecular decay that obeys the Lindemann mechanism is shown in Figure 14.21. This dependence is consistent with that which is experimentally observed in many unimolecular decompositions in the gas phase.

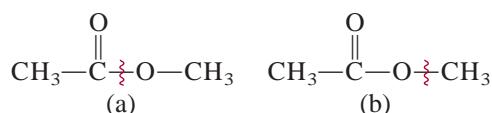
Experimental Support for Reaction Mechanisms

How can we find out whether the proposed mechanism for a particular reaction is correct? In the case of hydrogen peroxide decomposition, we might try to detect the presence of the IO^- ions by spectroscopic means. Evidence of their presence would support the reaction mechanism previously discussed. Similarly, for the hydrogen iodide reaction, the detection of iodine atoms would lend support to the two-step mechanism. For example, I_2 dissociates into I atoms when it is irradiated with visible light. Thus, we might predict that the formation of HI from H_2 and I_2 would speed up as the intensity of light is increased because that should increase the concentration of I atoms. Indeed, this is just what is observed.

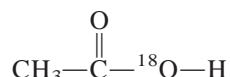
In one case, chemists wanted to know which C—O bond was broken in the reaction between methyl acetate and water in order to better understand the reaction mechanism.



The two possibilities are



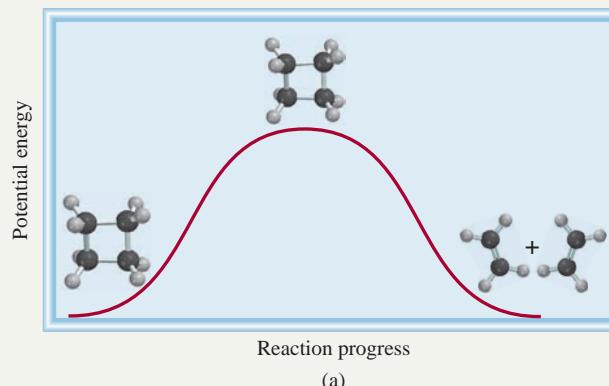
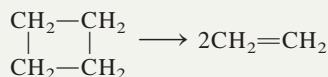
To distinguish between mechanisms (a) and (b), chemists used water containing the oxygen-18 isotope instead of ordinary water (which contains the oxygen-16 isotope). When the oxygen-18 water was used, only the acetic acid formed contained oxygen-18:



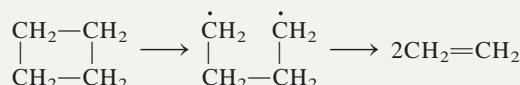
Femtochemistry

The ability to follow chemical reactions at the molecular level has been one of the most relentlessly pursued goals in chemistry. Accomplishing this goal will allow chemists to understand when a certain reaction occurs and the dependence of its rate of reaction on temperature and other parameters. On the practical side, this information will help chemists control reaction rates and increase reaction yields. A complete understanding of reaction mechanisms requires a detailed knowledge of the activated complex (also called the transition state). The transition state, however, is a highly energetic species that could not be isolated because of its extremely short lifetime.

The situation changed in the 1980s when researchers in the group of Ahmed Zewail at the California Institute of Technology began to use very short laser pulses to probe chemical reactions. Because transition states last only 10 to 1000 femtoseconds, the laser pulses needed to probe them must be extraordinarily short. [One femtosecond (1 fs) is 1×10^{-15} s. To appreciate how short this time duration is, note that there are as many femtoseconds in a second as there are seconds in about 32 million years!] One of the reactions studied was the decomposition of cyclobutane (C_4H_8) to ethylene (C_2H_4). There are two possible mechanisms. The first is a single-step process in which two carbon–carbon bonds break simultaneously to form the product:

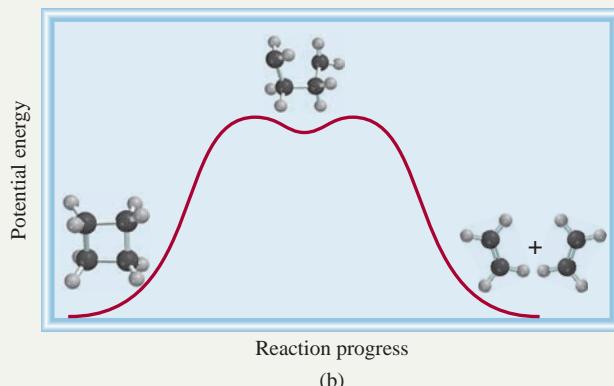


The second mechanism has two steps, with an intermediate where the dot represents an unpaired electron:



The Caltech researchers initiated the reaction with a pump laser pulse, which energized the reactant. The first probe pulse hit the molecules a few femtoseconds later and was followed by many thousands more, every 10 fs or so, for the duration of the reaction. Each probe pulse resulted in an absorption spectrum, and changes in the spectrum revealed the motion of the molecule and the state of the chemical bonds. In this way, the researchers were effectively equipped with a camera having different shutter speeds to capture the progress of the reaction. The results showed that cyclobutane decomposed to ethylene via the second (two-step) mechanism. The lifetime of the intermediate was about 700 fs.

The femtosecond laser technique has been used to unravel the mechanisms of many chemical reactions and biological processes such as photosynthesis and vision. It has created a new area in chemical kinetics that has become known as *femtochemistry*. For the development of the field of femtochemistry, Professor Zewail was awarded the Nobel Prize in Chemistry in 1999.



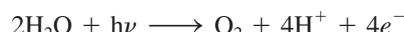
The decomposition of cyclobutane to form two ethylene molecules can take place in one of two ways. (a) The reaction proceeds via a single step, which involves the breaking of two C–C bonds simultaneously. (b) The reaction proceeds in two steps, with the formation of a shortlived intermediate in which just one bond is broken. There is only a small energy barrier for the intermediate to proceed to the final products. The correct mechanism is (b).

Thus, the reaction must have occurred via bond-breaking mechanism (a) because the product formed via mechanism (b) would retain both of its original oxygen atoms.

Now consider photosynthesis, the process by which green plants produce glucose from carbon dioxide and water:



A question that arose early in studies of photosynthesis was whether the molecular oxygen was derived from water, carbon dioxide, or both. By using water containing only the oxygen-18 isotope, it was demonstrated that the evolved oxygen came from water, and none came from carbon dioxide, because the O_2 contained only the ^{18}O isotope. This result supported the mechanism in which water molecules are “split” by light:



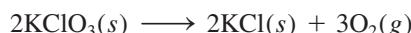
where $h\nu$ represents the energy of a photon. The protons and electrons are used to drive energetically unfavorable reactions that are necessary for plant growth and function.

These examples give some idea of how inventive chemists must be in studying reaction mechanisms. For complex reactions, however, it is virtually impossible to prove the uniqueness of any particular mechanism.

14.6 | Reaction Rates Can Often Be Increased by the Addition of a Catalyst

We saw in Section 14.5 that the reaction rate for the decomposition of hydrogen peroxide depends on the concentration of iodide ions even though I^- does not appear in the overall equation. Instead I^- acts as a catalyst for the reaction. A **catalyst** is a substance that increases the rate of a chemical reaction without itself being consumed.

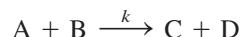
The catalyst may react to form an intermediate, but it is regenerated in a subsequent step of the reaction. In the laboratory preparation of molecular oxygen, for example, a sample of potassium chlorate is decomposed by heating, as follows



However, this thermal decomposition process is very slow in the absence of a catalyst. The rate of decomposition can be increased dramatically by adding a small amount of manganese dioxide (MnO_2), a black powdery substance that acts as a catalyst. All the MnO_2 can be recovered at the end of the reaction, just as all the I^- ions remain following the decomposition of H_2O_2 .

A catalyst speeds up a reaction by providing a set of elementary steps with more favorable kinetics than those that exist in its absence. From Equation 14.19, we know that the rate constant k (and hence the rate) of a reaction depends on the frequency factor A and the activation energy E_a —the larger the A or the smaller the E_a , the greater the rate. In many cases, a catalyst increases the rate by lowering the activation energy for the reaction.

Let us assume that the following reaction has a rate constant k and an activation energy E_a :



In the presence of a catalyst, however, the rate constant is k_c (called the *catalytic rate constant*):



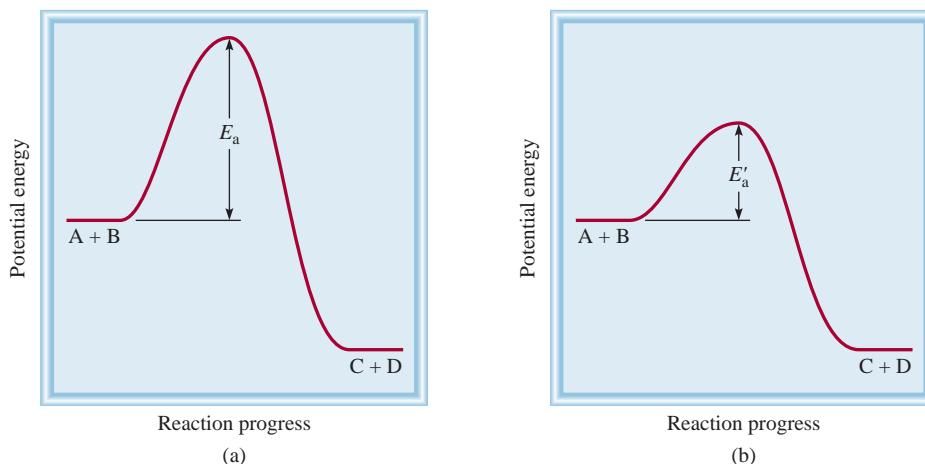


Figure 14.22 Comparison of the activation energy barriers of an uncatalyzed reaction and the same reaction with a catalyst. The catalyst lowers the energy barrier but does not affect the actual energies of the reactants or products. Although the reactants and products are the same in both cases, the reaction mechanisms and rate laws are different in (a) and (b).

By the definition of a catalyst,

$$\text{rate}_{\text{catalyzed}} > \text{rate}_{\text{uncatalyzed}}$$

Figure 14.22 shows the potential energy profiles for both reactions. The total energies of the reactants (A and B) and those of the products (C and D) are unaffected by the catalyst; the only difference between the two reactions is a lowering of the activation energy from E_a to E'_a . Because the activation energy for the reverse reaction is also lowered, a catalyst enhances the rates of the forward and reverse reactions equally.

There are three general types of catalysis, depending on the nature of the rate-increasing substance: heterogeneous catalysis, homogeneous catalysis, and enzyme catalysis.

Heterogeneous Catalysis

In **heterogeneous catalysis**, the reactants and the catalyst are in different phases. Usually the catalyst is a solid and the reactants are either gases or liquids. Heterogeneous catalysis is by far the most important type of catalysis in industrial chemistry, especially in the synthesis of many key chemicals. Here we describe three specific examples of heterogeneous catalysis that account for millions of tons of chemicals produced annually on an industrial scale.

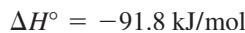
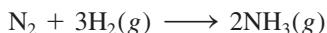
The Haber Synthesis of Ammonia

Ammonia is an extremely valuable inorganic substance used in the fertilizer industry, the manufacture of explosives, and many other applications. Around the turn of the century, many chemists strove to synthesize ammonia from nitrogen and hydrogen. The supply of atmospheric nitrogen is virtually inexhaustible, and hydrogen gas can be produced readily by passing steam over heated coal:



Hydrogen is also a by-product of petroleum refining.

The formation of NH_3 from N_2 and H_2 is exothermic:



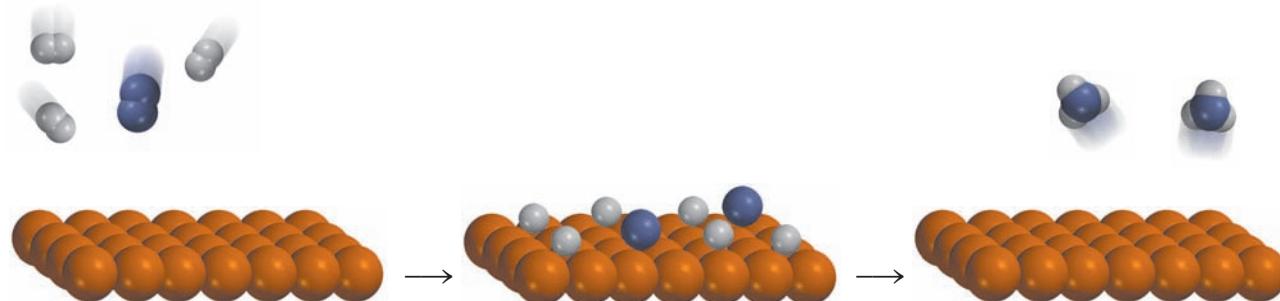


Figure 14.23 The catalytic action in the synthesis of ammonia. First, the H_2 and N_2 molecules bind to the surface of the catalyst. This interaction weakens the covalent bonds within the molecules and eventually causes the molecules to dissociate. Second, the highly reactive H and N atoms combine to form NH_3 molecules, which then leave the surface.

The reaction rate, however, is extremely slow at room temperature. To be practical on a large scale, a reaction must occur at an appreciable rate *and* it must have a high yield of the desired product. Raising the temperature does accelerate the reaction of N_2 with H_2 , but at the same time, it promotes the decomposition of NH_3 molecules back into N_2 and H_2 , thus lowering the yield of NH_3 .

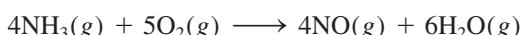
In 1905, after testing literally hundreds of compounds at various temperatures and pressures, Fritz Haber discovered that iron plus a few percent of oxides of potassium and aluminum catalyze the reaction of hydrogen with nitrogen to yield ammonia at about 500°C . This procedure is known as the *Haber process*.

In heterogeneous catalysis, the surface of the solid catalyst is usually the site of the reaction. The initial step in the Haber process is the dissociation of N_2 and H_2 on the metal surface (Figure 14.23). Although the dissociated species are not truly free atoms because they are bonded to the metal surface, they are highly reactive. The two reactant molecules behave very differently on the catalyst surface. Studies show that H_2 dissociates into atomic hydrogen at temperatures as low as -196°C (the boiling point of liquid nitrogen). Nitrogen molecules, on the other hand, dissociate at about 500°C . The highly reactive N and H atoms combine rapidly at high temperatures to produce the desired NH_3 molecules:

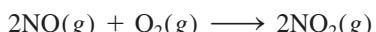


The Manufacture of Nitric Acid

Nitric acid is one of the most important inorganic acids. It is used in the production of fertilizers, dyes, drugs, and explosives. The major industrial method of producing nitric acid is the *Ostwald*⁴ process. The starting materials, ammonia and molecular oxygen, are heated in the presence of a platinum-rhodium catalyst (Figure 14.24) to about 800°C to produce nitric acid:



The nitric oxide readily oxidizes (without catalysis) to nitrogen dioxide:

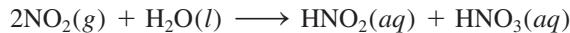


4. Wilhelm Ostwald (1853–1932). German chemist. Ostwald made important contributions to chemical kinetics, thermodynamics, and electrochemistry. He developed the industrial process for preparing nitric acid that now bears his name. He received the Nobel Prize in Chemistry in 1909.

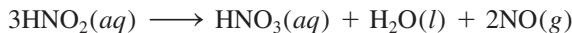


Figure 14.24 The platinum-rhodium catalyst used in the Ostwald process.

When dissolved in water, NO_2 forms both nitrous acid and nitric acid:



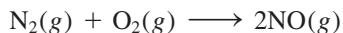
On heating, nitrous acid is converted to nitric acid as follows:



The NO thus generated can be recycled to produce NO_2 in the second step.

Catalytic Converters

At the high temperatures inside a running car engine, nitrogen and oxygen gases react to form nitric oxide:



When released into the atmosphere, NO rapidly combines with O_2 to form NO_2 . Nitrogen dioxide and other gases emitted by automobiles, such as carbon monoxide (CO) and various unburned hydrocarbons, make automobile exhaust a major source of air pollution.

All new cars are equipped with catalytic converters (Figure 14.25). An efficient catalytic converter serves two purposes: It oxidizes CO and unburned hydrocarbons to CO_2 and H_2O , and it reduces NO and NO_2 to N_2 and O_2 . Hot exhaust gases into which air has been injected are passed through the first chamber of one converter to

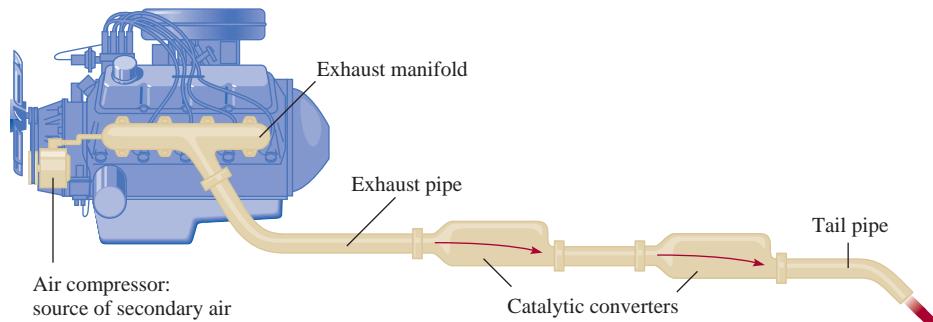
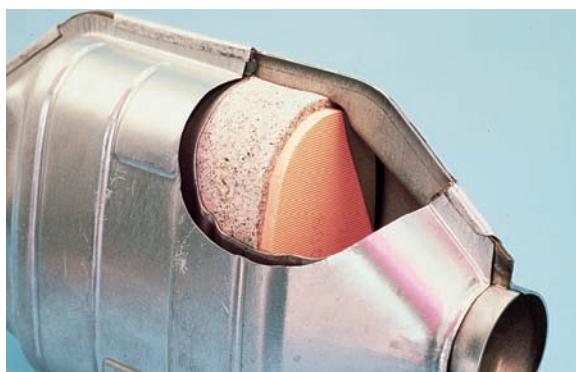


Figure 14.25 A two-stage catalytic converter for an automobile.

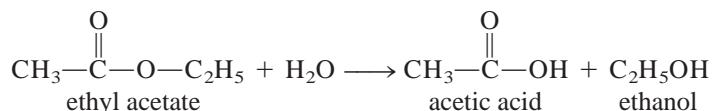
Figure 14.26 A catalytic converter (cross-sectional view). The beads contain platinum, palladium, and rhodium, which catalyze the combustion of CO and hydrocarbons.



accelerate the complete burning of hydrocarbons and to decrease CO emission. (A cross section of a catalytic converter is shown in Figure 14.26.) However, because high temperatures increase NO production, a second chamber containing a different catalyst (a transition metal or a transition metal oxide such as CuO or Cr₂O₃) and operating at a lower temperature is required to dissociate NO into N₂ and O₂ before the exhaust is discharged through the tailpipe.

Homogeneous Catalysis

In **homogeneous catalysis**, the reactants and catalyst are dispersed in a single phase, usually liquid. Acid catalysis and base catalysis are the most important types of homogeneous catalysis in liquid solution. For example, the reaction of ethyl acetate with water to form acetic acid and ethanol normally occurs too slowly to be measured



In the absence of the catalyst, the rate law is given by

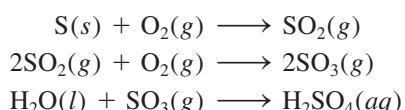
$$\text{rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5]$$

The reaction, however, can be catalyzed by an acid. In the presence of hydrochloric acid, the rate is faster and the rate law is given by

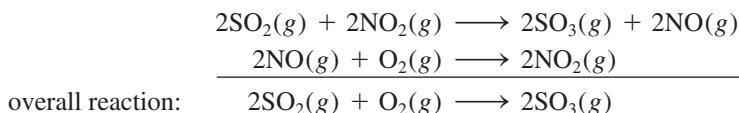
$$\text{rate} = k_c [\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}^+]$$

Because $k_c \geq k_r$, the rate is determined solely by the catalyzed portion of the reaction.

Homogeneous catalysis can also take place in the gas phase. A well-known example of catalyzed gas-phase reactions is the lead chamber process, which for many years was the primary method of manufacturing sulfuric acid. Starting with sulfur, one might expect the production of sulfuric acid to occur in the following steps:

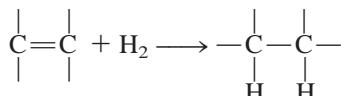


In reality, however, sulfur dioxide is not converted directly to sulfur trioxide; rather, the oxidation is more efficiently carried out in the presence of a nitrogen dioxide catalyst:



There is no net loss of NO_2 in the overall reaction, so NO_2 meets the criteria for a catalyst.

In recent years, chemists have devoted much effort to developing a class of metallic compounds to serve as homogeneous catalysts. These compounds are soluble in various organic solvents, so they can catalyze reactions in the same phase as the dissolved reactants. Many of the processes they catalyze are organic. For example, a red-violet compound of rhodium ($[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{RhCl}$) catalyzes the conversion of a carbon-carbon double bond to a carbon-carbon single bond as follows:



Homogeneous catalysis has several advantages over heterogeneous catalysis. For one thing, the reactions can often be carried out under atmospheric conditions, thus reducing production costs and minimizing the decomposition of products at high temperatures. In addition, homogeneous catalysts can be designed to function selectively for a particular type of reaction, and homogeneous catalysts cost less than the precious metals (for example, platinum and gold) used in heterogeneous catalysis.

Enzyme Catalysis

Of all the intricate processes that have evolved in living systems, none is more striking or more essential than enzyme catalysis. *Enzymes* are *biological catalysts*. The amazing fact about enzymes is that not only can they increase the rate of biochemical reactions by factors ranging from 10^6 to 10^{18} , but they are also highly specific. An enzyme acts only on certain molecules, called *substrates* (that is, reactants), while leaving the rest of the system unaffected. It has been estimated that an average living *cell* may contain some 3000 different enzymes, each of them catalyzing a specific reaction in which a substrate is converted into the appropriate products. Enzyme catalysis is usually homogeneous because the substrate and enzyme are present in the aqueous solution of the cell.

An enzyme is typically a large protein molecule that contains one or more *active sites* where interactions with substrates take place. These sites are structurally compatible with specific substrate molecules, in much the same way as a key fits a particular lock. In fact, the notion of a rigid enzyme structure that binds only to molecules whose shape exactly matches that of the active site was the basis of an early theory of enzyme catalysis, the so-called lock-and-key theory developed by the German chemist Emil Fischer⁵ in 1894 (Figure 14.27).

Fischer's hypothesis accounts for the specificity of enzymes, but it contradicts more recent research evidence that a single enzyme binds to substrates of different

5. Emil Fischer (1852–1919). German chemist. Regarded by many as the greatest organic chemist of the nineteenth century, Fischer made many significant contributions in the synthesis of sugars and other important molecules. He was awarded the Nobel Prize in Chemistry in 1902.

Figure 14.27 The lock-and-key model of the specificity of an enzyme for substrate molecules.

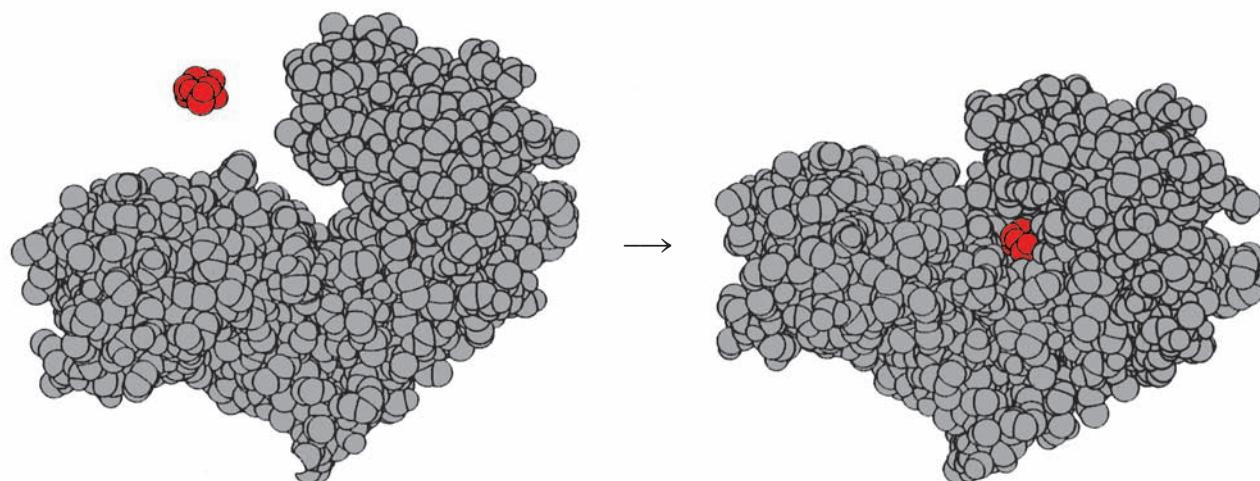
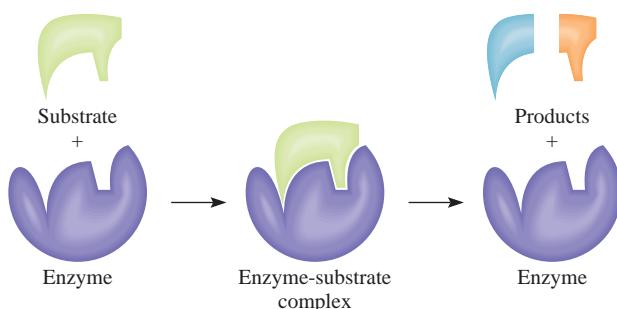


Figure 14.28 Left to right: The binding of a glucose molecule (red) to hexokinase (an enzyme in a metabolic pathway). Note how the region at the active site closes around glucose after binding. Frequently, the geometries of both the substrate and the active site are altered to fit each other. All enzymes possess a fair amount of flexibility.

sizes and shapes. Chemists now know that an enzyme molecule (or at least its active site) has a fair amount of structural flexibility and can modify its shape to accommodate more than one type of substrate. Figure 14.28 shows a molecular model of an enzyme in action.

In enzyme kinetics, it is customary to measure the *initial rate* (v_0) of a reaction to minimize the effect of reversible reactions and the inhibition of enzymes by products on the reaction rate. Furthermore, the initial rate corresponds to a known fixed substrate concentration. As time proceeds, the substrate concentration decreases.

Figure 14.29 shows the variation of the initial rate (v_0) of an enzyme-catalyzed reaction with substrate (S) concentration. The rate increases rapidly and linearly with [S] at low substrate concentrations, but it gradually levels off toward a limiting value at high substrate concentrations. In this region, all of the enzyme molecules are bound to the substrate molecules, and the rate becomes zero order in substrate concentration.

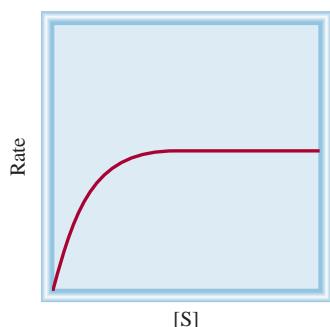


Figure 14.29 Plot of the initial rate (v_0) of an enzyme-catalyzed reaction versus substrate concentration.

The mathematical treatment of enzyme kinetics is quite complex, even when we know the basic steps involved in the reaction. The following simplified scheme, which

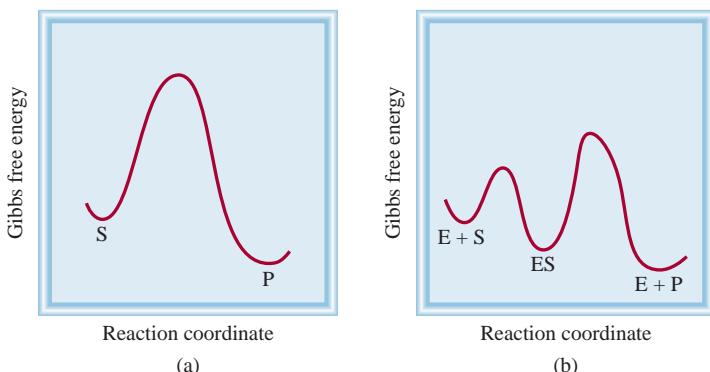
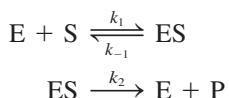


Figure 14.30 Comparison of the free energy profile for (a) an uncatalyzed reaction and (b) the same reaction catalyzed by an enzyme. The plot in (b) assumes that the catalyzed reaction has a two-step mechanism, in which the second step ($ES \rightarrow E + P$) is rate determining.

can explain the dependence of the rate on the substrate concentration (as shown in Figure 14.29) was proposed in 1913 by Michaelis⁶ and Menten⁷



where E, S, and P represent enzyme, substrate, and product, respectively, and ES is the enzyme-substrate intermediate. Figure 14.30 shows the free energy profile for the reaction compared to the reaction without a enzyme catalyst.

From the mechanism, the rate of formation of the product P is given by

$$\text{rate} = \frac{d[P]}{dt} = k_2[ES] \quad (14.35)$$

To give a useable rate law, we need to eliminate the concentration of the intermediate from Equation 14.35 using the steady-state approximation (Section 14.5). We start by setting the rate of formation of the intermediate ES to zero:

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES] = 0$$

Solving this equation for [ES] gives

$$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2} \quad (14.36)$$

Equation 14.36 can be written in terms of the easily measured initial concentration of enzyme $[E]_0$ by noting that the total amount of enzyme (bound and unbound) is conserved:

$$[E]_0 = [E] + [ES] \quad (14.37)$$

6. Leonor Michaelis (1875–1949). German biochemist and physician. In addition to his work with Menten on enzyme kinetics he made advances in microbiology and medicine. He made possible the permanent wave technique in hair care through his discovery that thioglycolic acid could dissolve keratin, the structural component of hair.

7. Maud L. Menten (1879–1960) Canadian biochemist. In addition to her work with Michaelis on enzyme kinetics, she characterized a number of bacterial toxins and was the first to separate proteins using electrophoresis.

Substituting Equation 14.37 into Equation 14.36 gives

$$[\text{ES}] = \frac{k_1}{k_{-1} + k_2} ([\text{E}]_0 - [\text{ES}])[\text{S}]$$

which gives, after rearrangement,

$$[\text{ES}] = \frac{[\text{E}]_0[\text{S}]}{K_M + [\text{S}]} \quad (14.38)$$

where

$$K_M = \frac{k_{-1} + k_2}{k_1}$$

is called the *Michaelis constant*. Substituting Equation 14.38 into the rate law (Equation 14.35) gives the *Michaelis-Menten equation* for enzyme kinetics:

$$\text{rate} = \frac{k_2[\text{E}]_0[\text{S}]}{K_M + [\text{S}]} \quad (14.39)$$

Thus, the rate is always proportional to the initial concentration of enzyme. If the substrate concentration is low (that is, $[\text{S}] \ll K_M$), then the Michaelis-Menten equation (Equation 14.39) reduces to

$$\text{rate} = (k_2/K_M)[\text{E}]_0[\text{S}]$$

which says that at low substrate concentration, the rate is directly proportional to the substrate concentration. This corresponds to the initial linear rise seen in Figure 14.29. On the other hand, if the substrate concentration is high (that is, $[\text{S}] \gg K_M$), Equation 14.39 becomes

$$\text{rate} = k_2[\text{E}]_0$$

that is, the rate becomes independent of $[\text{S}]$. This is seen in Figure 14.29 as a leveling off of the rate at high $[\text{S}]$. Thus, we see that the Michaelis-Menten reaction mechanism correctly describes the experimentally observed rate data for enzyme kinetics.

Summary of Facts and Concepts

Section 14.1

- The rate of a chemical reaction is the change in the concentration of reactants or products over time. The rate is not constant, but varies continuously as concentrations change.

Section 14.2

- The rate law expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to appropriate powers. The rate constant k for a given reaction changes only with temperature.
- Reaction order is the power to which the concentration of a given reactant is raised in the rate law. The overall

reaction order is the sum of the powers to which reactant concentrations are raised in the rate law. The rate law and the reaction order cannot be determined from the stoichiometry of the overall equation for a reaction; they must be determined by experiment. For a zero-order reaction, the reaction rate is equal to the rate constant.

Section 14.3

- The rate law for a reaction can be integrated to determine the concentrations of reactants and products as functions of time.
- The half-life of a reaction (the time it takes for the concentration of a reactant to decrease by one-half)

can be used to determine the rate constant of a first-order reaction.

Section 14.4

- ▶ In terms of collision theory, a reaction occurs when molecules collide with sufficient energy, called the activation energy, to break the bonds and initiate the reaction. The rate constant and the activation energy are related by the Arrhenius equation.
- ▶ The activation energy can be determined from the temperature dependence of the rate constant.
- ▶ In a reversible reaction, the equilibrium constant can be determined from the ratio of the forward and reverse reaction rates.

Section 14.5

- ▶ The overall balanced equation for a reaction may be the sum of a series of simple reactions, called elementary

steps. The complete series of elementary steps for a reaction is the reaction mechanism.

- ▶ The rate law for a given reaction can be determined if the mechanism is known; however, because a number of possible mechanisms can give the same rate law, it is not generally possible to determine the mechanism directly from the rate law alone—additional experiments are necessary.
- ▶ If one step in a reaction mechanism is much slower than all other steps, it is the rate-determining step.

Section 14.6

- ▶ A catalyst speeds up a reaction usually by lowering the value of E_a without being consumed in the net reaction.
- ▶ In heterogeneous catalysis, the catalyst is a solid and the reactants are gases or liquids. In homogeneous catalysis, the catalyst and the reactants are in the same phase. Enzymes are catalysts in living systems.

Key Words

activated complex, p. 739

activated-complex theory, p. 742

activation energy, p. 736

bimolecular, p. 744

catalyst, p. 754

chemical kinetics, p. 713

detailed balance, p. 735

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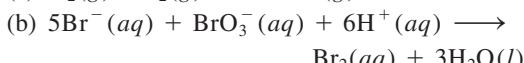
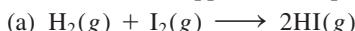
transition-state theory, p. 742

unimolecular, p. 744

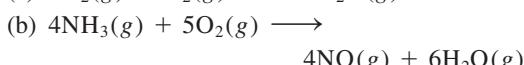
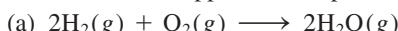
Problems

Chemical Kinetics Is the Study of the Rates at Which Chemical Reactions Occur

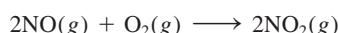
- 14.1 Write the reaction rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of products:



- 14.2 Write the reaction rate expressions for the following reactions in terms of the disappearance of the reactants and the appearance of products:

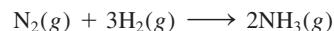


- 14.3 Consider the reaction



Suppose that at a particular moment during the reaction nitric oxide (NO) is reacting at the rate of 0.066 M s^{-1} . (a) At what rate is NO_2 being formed? (b) At what rate is molecular oxygen reacting?

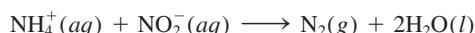
- 14.4 Consider the reaction



Suppose that at a particular moment during the reaction molecular hydrogen is reacting at the rate of 0.074 M s^{-1} . (a) At what rate is ammonia being formed? (b) At what rate is molecular nitrogen reacting?

The Rate Law Gives the Dependence of the Reaction Rate on the Reactant Concentrations

- 14.5 The rate law for the reaction



is given by rate = $k [\text{NH}_4^+] [\text{NO}_2^-]$. At 25°C, the rate constant is $3.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$. Calculate the rate of the reaction at this temperature if $[\text{NH}_4^+] = 0.26 \text{ M}$ and $[\text{NO}_2^-] = 0.080 \text{ M}$.

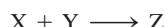
- 14.6 Use the data in Table 14.2 to calculate the rate of the reaction at the time when $[\text{F}_2] = 0.010 \text{ M}$ and $[\text{ClO}_2] = 0.020 \text{ M}$.
- 14.7 Consider the reaction



From the following data obtained at a certain temperature, determine the order of the reaction and calculate the rate constant:

| [A] (M) | [B] (M) | Rate (M s ⁻¹) |
|---------|---------|---------------------------|
| 1.50 | 1.50 | 3.20×10^{-1} |
| 1.50 | 2.50 | 3.20×10^{-1} |
| 3.00 | 1.50 | 6.40×10^{-1} |

- 14.8 Consider the reaction



From the following data, obtained at 360 K, (a) determine the order of the reaction, and (b) determine the initial rate of disappearance of X when the concentration of X is 0.30 M and the concentration of Y is 0.40 M.

| [X] (M) | [Y] (M) | Initial Rate of Disappearance of X (M s ⁻¹) |
|---------|---------|---|
| 0.10 | 0.50 | 0.053 |
| 0.20 | 0.30 | 0.127 |
| 0.40 | 0.60 | 1.02 |
| 0.20 | 0.60 | 0.254 |
| 0.40 | 0.30 | 0.509 |

- 14.9 Determine the overall orders of the reactions to which the following rate laws apply: (a) rate = $k[\text{NO}_2]^2$, (b) rate = k , (c) rate = $k[\text{H}_2][\text{Br}_2]^{1/2}$, and (d) rate = $k[\text{NO}]^2[\text{O}_2]$.
- 14.10 What are the units of the rate constant for a third-order reaction?
- 14.11 Consider the reaction A → B. The rate of the reaction is $1.6 \times 10^{-2} \text{ M s}^{-1}$ when the concentration of A is 0.35 M. Calculate the rate constant if the reaction is (a) first order in A and (b) second order in A.
- 14.12 Cyclobutane decomposes to ethylene according to the following equation:



Determine the order of the reaction and the rate constant based on the following pressures, which were recorded when the reaction was carried out at 430°C in a constant-volume vessel.

| Time (s) | P _{C₄H₈} (mmHg) |
|----------|--|
| 0 | 400 |
| 2,000 | 316 |
| 4,000 | 248 |
| 6,000 | 196 |
| 8,000 | 155 |
| 10,000 | 122 |

- 14.13 The following gas-phase reaction was studied at 290°C by observing the change in pressure as a function of time in a constant-volume vessel:



Determine the order of the reaction and the rate constant based on the following data:

| Time (s) | P (mmHg) |
|----------|----------|
| 0 | 15.76 |
| 181 | 18.88 |
| 513 | 22.79 |
| 1164 | 27.08 |

where P is the total pressure.

Integrated Rate Laws Specify the Relationship Between Reactant Concentration and Time

- 14.14 What is the half-life of a compound if 75 percent of a given sample of the compound decomposes in 60 min? Assume first-order kinetics.
- 14.15 A certain first-order reaction is 35.5 percent complete in 49 min at 298 K. What is the rate constant at this temperature?
- 14.16 The thermal decomposition of phosphine (PH_3) into phosphorus and molecular hydrogen is a first-order reaction:



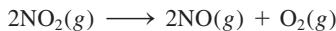
The half-life of the reaction is 35.0 s at 680°C. Calculate (a) the first-order rate constant for the reaction and (b) the time required for 95 percent of the phosphine to decompose.

- 14.17 The rate constant for the second-order reaction



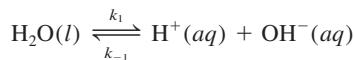
is $0.80 \text{ M}^{-1} \text{ s}^{-1}$ at 10°C. (a) Starting with a concentration of 0.086 M, calculate the concentration of NOBr after 22 s. (b) Calculate the half-lives when $[\text{NOBr}]_0 = 0.072 \text{ M}$ and when $[\text{NOBr}]_0 = 0.054 \text{ M}$.

- 14.18 The rate constant for the second-order reaction



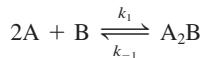
is $0.54 \text{ M}^{-1} \text{ s}^{-1}$ at 300°C . How long (in seconds) would it take for the concentration of NO_2 to decrease from 0.62 M to 0.28 M ?

- 14.19 If the first half-life of a zero-order reaction is 200 s, what will be the duration of the next half-life?
- 14.20 A reaction $\text{A} + \text{B} \longrightarrow \text{C}$ is first order in both A and B and second order overall with a rate constant of $0.0500 \text{ M}^{-1} \text{ s}^{-1}$. If the initial concentration of A is 1.00 M , the initial concentration of B is 0.500 M , and no product is initially present, what is the concentration of the product C after 2 minutes? After 10 minutes?
- 14.21 Water is a very weak electrolyte that undergoes the following ionization (called autoionization):



(a) If $k_1 = 2.3 \times 10^{-5} \text{ s}^{-1}$ and $k_{-1} = 1.3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, calculate the value of the equilibrium constant $K = [\text{H}^+][\text{OH}^-]/[\text{H}_2\text{O}]$. (b) Calculate the product $[\text{H}^+][\text{OH}^-]$ and $[\text{H}^+]$ and $[\text{OH}^-]$.

- 14.22 Consider the following reaction, which takes place in a single elementary step:



If the equilibrium constant K_c is 12.6 at a certain temperature and k_{-1} is $5.1 \times 10^{-2} \text{ s}^{-1}$, calculate the value of k_1 .

The Arrhenius Equation Gives the Temperature Dependence of Rate Constants

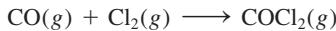
- 14.23 The variation of the rate constant with temperature for the first-order reaction



is given in the table. Determine graphically the activation energy for the reaction.

| $T \text{ (K)}$ | $k \text{ (s}^{-1}\text{)}$ |
|-----------------|-----------------------------|
| 298 | 1.74×10^{-5} |
| 308 | 6.61×10^{-5} |
| 318 | 2.51×10^{-4} |
| 328 | 7.59×10^{-4} |
| 338 | 2.40×10^{-3} |

- 14.24 Given the same reactant concentrations, the reaction



at 250°C is 1.50×10^3 times as fast as the same reaction at 150°C . Calculate the activation energy for this reaction. Assume that the frequency factor is constant.

- 14.25 For the reaction

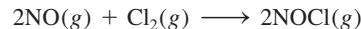


the frequency factor A is $8.7 \times 10^{12} \text{ s}^{-1}$ and the activation energy is 63 kJ mol^{-1} . What is the rate constant for the reaction at 75°C ?

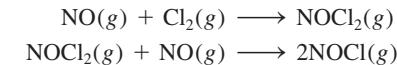
- 14.26 The rate constant of a first-order reaction is $4.60 \times 10^{-4} \text{ s}^{-1}$ at 350°C . If the activation energy is 104 kJ mol^{-1} , calculate the temperature at which its rate constant is $8.80 \times 10^{-4} \text{ s}^{-1}$.
- 14.27 The rate constants of some reactions double with every 10°C rise in temperature. Assume that a reaction takes place at 295 K and 305 K . What must the activation energy be for the rate constant to double as described?
- 14.28 The rate at which tree crickets chirp is 2.0×10^2 per minute at 27°C but only 39.6 per minute at 5°C . From these data, calculate the “activation energy” for the chirping process. (*Hint:* The ratio of rates is equal to the ratio of rate constants.)
- 14.29 The rate of bacterial hydrolysis of fish muscle is twice as great at 2.2°C as at -1.1°C . Estimate the value of the activation energy for this reaction. Is there any relation to the problem of storing fish for food? [Source: J.A. Campbell, Eco-Chem. *J. Chem. Ed.* 52, 390 (1975).]
- 14.30 The gas-phase reaction $\text{X} \longrightarrow \text{Y}$ has a reaction enthalpy of -64 kJ mol^{-1} and an activation energy of 22 kJ mol^{-1} . What is the activation energy of the reaction $\text{Y} \longrightarrow \text{X}'$?

The Reaction Mechanism Is the Sequence of Elementary Steps That Lead to Product Formation

- 14.31 The rate law for the reaction



is given by rate $k[\text{NO}][\text{Cl}_2]$. (a) What is the order of the reaction? (b) A mechanism involving the following steps has been proposed for the reaction:



If this mechanism is correct, what does it imply about the relative rates of these two steps?

- 14.32 For the reaction



it is found that doubling the concentration of X_2 doubles the reaction rate, tripling the concentration of Y triples the rate, and doubling the concentration of Z has no effect. (a) What is the rate law for this reaction? (b) Why is it that the change in the concentration of Z has no effect on the rate? (c) Suggest a mechanism for the reaction that is consistent with the rate law.

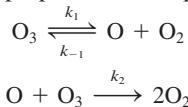
- 14.33 The rate law for the decomposition of ozone to molecular oxygen



is

$$\text{rate} = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

The mechanism proposed for this process is



(a) Derive the rate law from these elementary steps assuming that rapid preequilibrium is established in the first step. Explain why the rate decreases with increasing O_2 concentration. (b) Repeat the derivation using the steady-state approximation. What does the experimental rate law tell you about the relative magnitudes of the rate constants in this case?

- 14.34 The rate law for the reaction

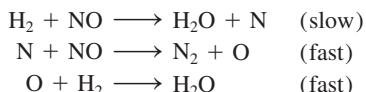


is

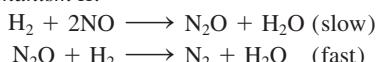
$$\text{rate} = k[\text{H}_2][\text{NO}]^2$$

Which of the following mechanisms can be ruled out on the basis of the observed rate expression?

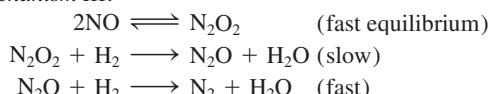
mechanism I:



mechanism II:



mechanism III:



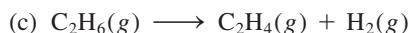
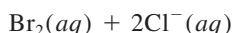
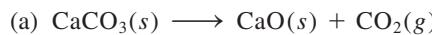
Reaction Rates Can Often Be Increased by the Addition of a Catalyst

- 14.35 Most reactions, including enzyme-catalyzed reactions, proceed faster at higher temperatures. For a given enzyme, however, the rate drops off abruptly at a certain temperature. Account for this behavior.

- 14.36 Use the rapid preequilibrium approximation to derive the Michaelis-Menten mechanism for enzyme catalysis (Equation 14.39).

Additional Problems

- 14.37 Suggest experimental means by which the rates of the following reactions could be followed:



- 14.38 List four factors that influence the rate of a reaction.

- 14.39 “The rate constant for the reaction



is $1.64 \times 10^{-6} \text{ M}^{-1} \text{ s.}$ ” What is incomplete about this statement?

- 14.40 In a certain industrial process involving a heterogeneous catalyst, the volume of the catalyst (in the shape of a sphere) is 10.0 cm^3 . Calculate the surface area of the catalyst. If the sphere is broken down into eight spheres, each having a volume of 1.25 cm^3 , what is the total surface area of the spheres? Which of the two geometric configurations of the catalyst is more effective? (The surface area of a sphere is $4\pi r^2$, where r is the radius of the sphere.) Based on your analysis here, explain why it is sometimes dangerous to work in grain elevators.

- 14.41 Use the data in Example 14.4 to determine graphically the half-life of the reaction.

- 14.42 The following data were collected for the reaction between hydrogen and nitric oxide at 700°C :



| Experiment | [H ₂] | [NO] | Initial Rate (M s ⁻¹) |
|------------|-------------------|--------|-----------------------------------|
| 1 | 0.010 | 0.025 | 2.4×10^{-6} |
| 2 | 0.0050 | 0.025 | 1.2×10^{-6} |
| 3 | 0.010 | 0.0125 | 0.60×10^{-6} |

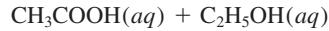
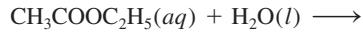
(a) Determine the order of the reaction. (b) Calculate the rate constant. (c) Suggest a plausible mechanism that is consistent with the rate law. (*Hint:* Assume that the oxygen atom is the intermediate.)

- 14.43 When methyl phosphate is heated in acid solution, it reacts with water:



If the reaction is carried out in water enriched with ¹⁸O, the oxygen-18 isotope is found in the phosphoric acid product but not in the methanol. What does this tell us about the mechanism of the reaction?

- 14.44 The rate of the reaction

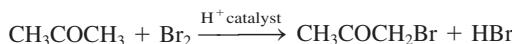


shows first-order characteristics—that is, rate = $k[\text{CH}_3\text{COOC}_2\text{H}_5]$ —even though it is a second-order reaction (first order in $\text{CH}_3\text{COOC}_2\text{H}_5$ and first order in H_2O). Explain.

14.45 Explain why most metals used in catalysis are transition metals.

14.46 The reaction $2A + 3B \rightarrow C$ is first order with respect to A and B. When the initial concentrations are $[A] = 1.6 \times 10^{-2} M$ and $[B] = 2.4 \times 10^{-3} M$, the rate is $4.1 \times 10^{-4} M s^{-1}$. Calculate the rate constant of the reaction.

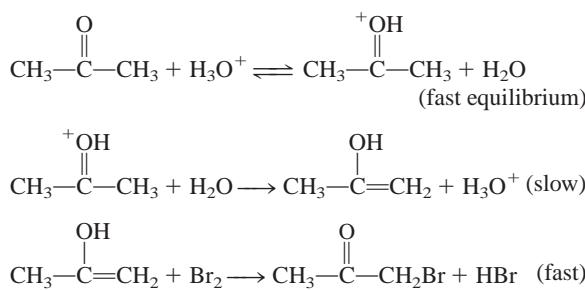
14.47 The bromination of acetone is acid-catalyzed:



The rate of disappearance of bromine was measured for several different concentrations of acetone, bromine, and H^+ ions at a certain temperature:

| Experiment | $[\text{CH}_3\text{COCH}_3]$ | $[\text{Br}_2]$ | $[\text{H}^+]$ | Rate of Disappearance of $\text{Br}_2 (M s^{-1})$ |
|------------|------------------------------|-----------------|----------------|---|
| 1 | 0.30 | 0.050 | 0.050 | 5.7×10^{-5} |
| 2 | 0.30 | 0.10 | 0.050 | 5.7×10^{-5} |
| 3 | 0.30 | 0.050 | 0.10 | 1.2×10^{-4} |
| 4 | 0.40 | 0.050 | 0.20 | 3.1×10^{-4} |
| 5 | 0.40 | 0.050 | 0.050 | 7.6×10^{-5} |

(a) What is the rate law for the reaction? (b) Determine the rate constant. (c) The following mechanism has been proposed for the reaction:



Show that the rate law deduced from the mechanism is consistent with that shown in (a).

14.48 The decomposition of N_2O to N_2 and O_2 is a first-order reaction. At 730°C , the half-life of the reaction is 3.58×10^3 min. If the initial pressure of N_2O is 2.10 bar at 730°C , calculate the total gas pressure after one half-life. Assume ideal gas behavior and that the volume remains constant.

14.49 The reaction



proceeds slowly in aqueous solution, but it can be catalyzed by the Fe^{3+} ion. Given that Fe^+ can oxidize I^- and Fe^{3+} can reduce $\text{S}_2\text{O}_8^{2-}$, write a plausible two-step mechanism for this reaction. Explain why the uncatalyzed reaction is slow.

14.50 The rate constants for the first-order decomposition of a organic compound in solution has been measured at several temperatures

| | | | | | |
|--------------------|-----------------------|--------|--------|-------|------|
| $k(\text{s}^{-1})$ | 4.92×10^{-3} | 0.0216 | 0.0950 | 0.326 | 1.15 |
| $T^\circ\text{C}$ | 5.0 | 15 | 25 | 35 | 45 |

Determine graphically the preexponential factor and the energy of activation for the reaction.

14.51 A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives are 50.0 min for A and 18.0 min for B. If the concentrations of A and B are equal initially, how long will it take for the concentration of A to be four times that of B?

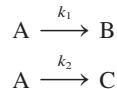
14.52 Referring to Example 14.4, explain how you would measure the partial pressure of azomethane experimentally as a function of time.

14.53 The rate law for the reaction



is rate = $k[\text{NO}_2]^2$. Which of the following changes will change the value of k ? (a) The pressure of NO_2 is doubled. (b) The reaction is run in an organic solvent. (c) The volume of the container is doubled. (d) The temperature is decreased. (e) A catalyst is added to the container.

14.54 Consider the following parallel reactions



The activation energies are 27.2 kJ mol⁻¹ for k_1 and 49.6 kJ mol⁻¹ for k_2 . At what temperature would $k_1/k_2 = 1.50$ given that the rate constants are equal at 400 K.

14.55 Consider the parallel reactions in Problem 14.54. If $[\text{A}]_0$ denotes the initial concentration of A, determine the ratio $[\text{B}]/[\text{C}]$ upon completion of the reaction in terms of the rate constants k_1 and k_2 , assuming that B and C are not present initially.

14.56 The reaction of G_2 with E_2 to form 2EG is exothermic, and the reaction of G_2 with X_2 to form 2XG is endothermic. The activation energy of the exothermic reaction is greater than that of the endothermic reaction. Sketch the potential energy profile diagrams for these two reactions on the same graph.

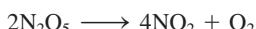
14.57 Briefly comment on the effect of a catalyst on each of the following: (a) activation energy, (b) reaction mechanism, (c) enthalpy of reaction, (d) rate of forward step, and (e) rate of reverse step.

14.58 When 6 g of granulated Zn is added to a solution of 2 M HCl in a beaker at room temperature, hydrogen gas is generated. For each of the following changes (at constant volume of the acid), state whether the

rate of hydrogen gas evolution will be increased, decreased, or unchanged: (a) 6 g of powdered Zn is used; (b) 4 g of granulated Zn is used; (c) 2 M acetic acid is used instead of 2 M HCl; and (d) temperature is raised to 40°C.

- 14.59 Strictly speaking, the rate law derived for the reaction in Problem 14.42 applies only to certain concentrations of H₂. The general rate law for the reaction takes the form where k_1 and k_2 are constants. Derive rate law expressions under the conditions of very high and very low hydrogen concentrations. Does the result from Problem 14.42 agree with one of the rate expressions here?

- 14.60 The decomposition of dinitrogen pentoxide



has been studied in carbon tetrachloride (CCl₄) solvent at a certain temperature and the following results were obtained:

| [N ₂ O ₅] | Initial Rate (M s ⁻¹) |
|----------------------------------|-----------------------------------|
| 0.92 | 0.95 × 10 ⁻⁵ |
| 1.23 | 1.20 × 10 ⁻⁵ |
| 1.79 | 1.93 × 10 ⁻⁵ |
| 2.00 | 2.10 × 10 ⁻⁵ |
| 2.21 | 2.26 × 10 ⁻⁵ |

Determine graphically the rate law for the reaction and calculate the rate constant.

- 14.61 The thermal decomposition of N₂O₅ obeys first-order kinetics. At 45°C, a plot of ln[N₂O₅] versus t gives a slope of 6.18×10^{-4} min⁻¹. What is the half-life of the reaction?

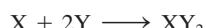
- 14.62 When a mixture of methane and bromine is exposed to light, the following reaction occurs slowly:



Suggest a reasonable mechanism for this reaction. (*Hint:* Bromine vapor is deep red; methane is colorless.)

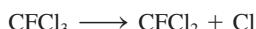
- 14.63 The rate of the reaction between H₂ and I₂ to form HI (discussed on p. 748) increases with the intensity of visible light. (a) Explain why this fact supports the two-step mechanism given. (The color of I₂ vapor is shown on p. 748.) (b) Explain why visible light has no effect on the formation of H atoms.

- 14.64 Consider the following elementary step:



(a) Write a rate law for this reaction. (b) If the initial rate of formation of XY₂ is 3.8×10^{-3} M s⁻¹ and the initial concentrations of X and Y are 0.26 M and 0.88 M, respectively, what is the rate constant of the reaction?

- 14.65 In recent years, ozone in the stratosphere has been depleted at an alarmingly fast rate by chlorofluorocarbons (CFCs). A CFC molecule such as CFCl₃ is first decomposed by UV radiation:



The chlorine radical then reacts with ozone as follows:



- (a) Write the overall reaction for the last two steps. (b) What are the roles of Cl and ClO? (c) Why is the fluorine radical not important in this mechanism? (d) One suggestion to reduce the concentration of chlorine radicals is to add hydrocarbons such as ethane (C₂H₆) to the stratosphere. How will this work? (e) Draw potential energy versus reaction progress diagrams for the uncatalyzed and catalyzed (by Cl) destruction of ozone: O₃ + O → 2O₂. Use the thermodynamic data in Appendix 2 to determine whether the reaction is exothermic or endothermic.

- 14.66 Chlorine oxide (ClO), which plays an important role in the depletion of stratospheric ozone (see Problem 14.65), decays rapidly at room temperature according to the following equation



From the following data, determine the reaction order and calculate the rate constant of the reaction

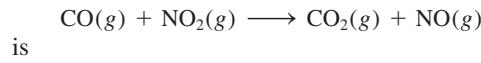
| Time (s) | [ClO] (M) |
|-----------------------|-----------------------|
| 0.12×10^{-3} | 8.49×10^{-6} |
| 0.96×10^{-3} | 7.10×10^{-6} |
| 2.24×10^{-3} | 5.79×10^{-6} |
| 3.20×10^{-3} | 5.20×10^{-6} |
| 4.00×10^{-3} | 4.77×10^{-6} |

- 14.67 A compound X undergoes two parallel first-order reactions as follows: X → Y with rate constant k_1 and X → Z with rate constant k_2 . The ratio of k_1/k_2 at 40°C is 8.0. What is the ratio at 300°C? Assume that the frequency factors of the two reactions are the same.

- 14.68 Consider a car fitted with a catalytic converter. The first 5 min or so after it is started are the most polluting. Why?

- 14.69 (a) What can you deduce about the activation energy of a reaction if its rate constant changes significantly with a small change in temperature? (b) If a bimolecular reaction occurs every time an A and a B molecule collide, what can you say about the orientation factor and activation energy of the reaction?

- 14.70 The rate law for the reaction



$$\text{rate} = k[\text{NO}_2]^2$$

Suggest a plausible mechanism for the reaction, given that the unstable species NO_3 is an intermediate.

- 14.71 Many reactions involving heterogeneous catalysts are zero order, that is, $\text{rate} = k$. An example is the decomposition of phosphine (PH_3) over tungsten (W):

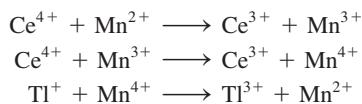


It is found that the reaction is independent of $[\text{PH}_3]$ as long as phosphine's pressure is sufficiently high (≥ 1 bar). Explain.

- 14.72 Thallium(I) is oxidized by cerium(IV) as follows:

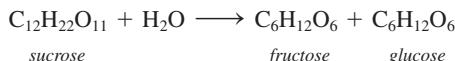


The elementary steps, in the presence of Mn(II), are as follows:



(a) Identify the catalyst, intermediates, and the rate-determining step if the rate law is $\text{rate} = k[\text{Ce}^{4+}][\text{Mn}^{2+}]$. (b) Explain why the reaction is slow without the catalyst. (c) Is the catalysis homogeneous or heterogeneous?

- 14.73 Sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), commonly called table sugar, undergoes hydrolysis (reaction with water) to produce fructose ($\text{C}_6\text{H}_{12}\text{O}_6$) and glucose ($\text{C}_6\text{H}_{12}\text{O}_6$):



This reaction is of considerable importance in the candy industry for at least two reasons. First, fructose is sweeter than sucrose, so the same level of sweetness can be achieved with fewer raw materials if fructose is substituted for sucrose. Second, a mixture of fructose and glucose, called *invert sugar*, does not crystallize, so the candy containing this sugar would be chewy rather than brittle as candy containing sucrose crystals would be. (a) From the following data, determine the order of the reaction. (b) How long does it take to hydrolyze 95 percent of the sucrose? (c) Explain why the rate law does not include $[\text{H}_2\text{O}]$ even though water is a reactant.

| Time (min) | $[\text{C}_{12}\text{H}_{22}\text{O}_{11}] (\text{M})$ |
|------------|--|
| 0 | 0.500 |
| 60.0 | 0.400 |
| 96.4 | 0.350 |
| 157.5 | 0.280 |

- 14.74 The first-order rate constant for the decomposition of dimethyl ether

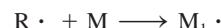


is $3.2 \times 10^{-4} \text{ s}^{-1}$ at 450°C . The reaction is carried out in a constant-volume flask. Initially only dimethyl ether is present and the pressure is 0.350 bar. What is the pressure of the system after 8.0 min? Assume ideal gas behavior.

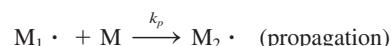
- 14.75 Polyethylene is used in many items, including water pipes, bottles, electrical insulation, toys, and mailer envelopes. It is a *polymer*, a molecule with a very high molar mass made by joining many ethylene molecules together. (Ethylene is the basic unit, or monomer, for polyethylene.) The initiation step is



The $\text{R}\cdot$ species (called a radical) reacts with an ethylene molecule (M) to generate another radical



The reaction of $\text{M}_1\cdot$ with another monomer leads to the growth or propagation of the polymer chain:



This step can be repeated with hundreds of monomer units. The propagation terminates when two radicals combine

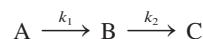


- (a) The initiator frequently used in the polymerization of ethylene is benzoyl peroxide $[(\text{C}_6\text{H}_5\text{COO})_2]$:



This is a first-order reaction. The half-life of benzoyl peroxide at 100°C is 19.8 min. Calculate the rate constant (in min^{-1}) of the reaction. (b) If the half-life of benzoyl peroxide is 7.30 h (438 min) at 70°C , what is the activation energy (in kJ mol^{-1}) for the decomposition of benzoyl peroxide? (c) Write the rate laws for the elementary steps in the polymerization of ethylene, and identify the reactant, product, and intermediates. (d) What condition would favor the growth of long, high-molar-mass polyethylenes?

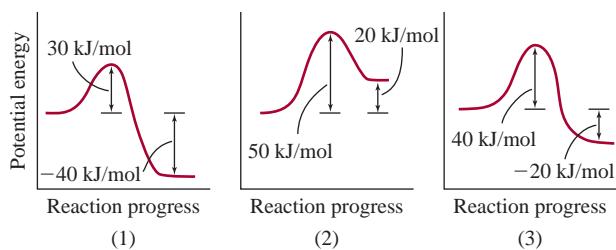
- 14.76 Consider the following elementary steps for a consecutive reaction:



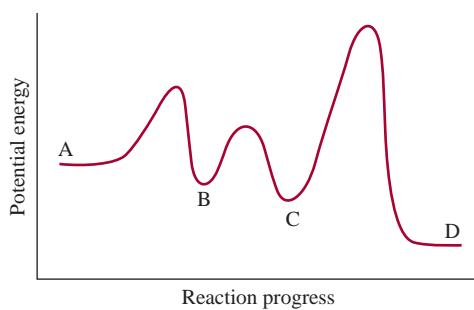
- (a) Write an expression for the rate of change of B.
 (b) Derive an expression for the concentration of B under steady-state conditions that is, when B is decomposing to C at the same rate as it is formed from A. (c) Compare the expression derived in (b) to the Equation 14.16 derived in Section 14.3.

- 14.77 Ethanol is a toxic substance that, when consumed in excess, can impair respiratory and cardiac functions by interfering with the neurotransmitters of the nervous system. In the human body, ethanol is metabolized by the enzyme alcohol dehydrogenase to acetaldehyde, which causes “hangovers.” (a) Based on your knowledge of enzyme kinetics, explain why binge drinking (i.e., consuming too much alcohol too fast) can prove fatal. (b) Methanol is even more toxic than ethanol. It is also metabolized by alcohol dehydrogenase, and the product, formaldehyde, can cause blindness or death. An antidote to methanol poisoning is ethanol. Explain how this procedure works.

- 14.78 Consider the potential energy profiles for the following three reactions (from left to right). (a) Rank the rates of the reactions from slowest to fastest. (b) Calculate ΔH for each reaction and determine which reaction(s) are exothermic and which reaction(s) are endothermic. Assume the reactions have roughly the same frequency factors.

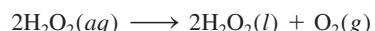


- 14.79 Consider the following potential energy profile for the $A \rightarrow D$ reaction. (a) How many elementary steps are there? (b) How many intermediates are formed? (c) Which step is rate determining? (d) Is the overall reaction exothermic or endothermic?



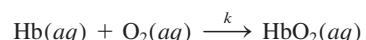
- 14.80 A factory that specializes in the refinement of transition metals such as titanium was on fire. The firefighters were advised not to douse the fire with water. Why?

- 14.81 The activation energy for the decomposition of hydrogen peroxide



is 42 kJ mol^{-1} , whereas it is 7.0 kJ mol^{-1} when the reaction is catalyzed by the enzyme catalase. Calculate the temperature that would cause the nonenzymatic catalysis to proceed as rapidly as the enzyme-catalyzed decomposition at 20°C . Assume the frequency factor A is the same in both cases.

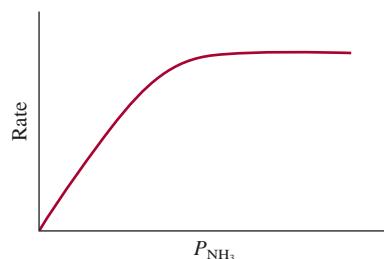
- 14.82 To carry out metabolism, oxygen is taken up by hemoglobin (Hb) to form oxyhemoglobin (HbO_2) according to the following simplified equation



where the second-order rate constant is $2.1 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ at 37°C . For an average adult, the concentrations of Hb and O_2 in the blood at the lungs are $8.0 \times 10^{-6} \text{ M}$ and $1.5 \times 10^{-6} \text{ M}$, respectively.

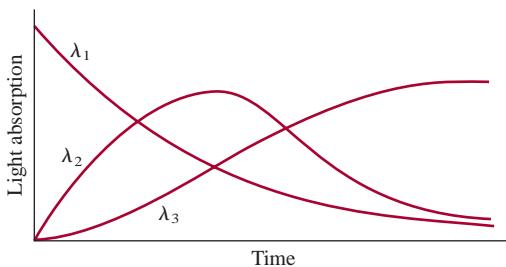
(a) Calculate the rate of formation of HbO_2 . (b) Calculate the rate of consumption of O_2 . (c) The rate of formation of HbO_2 increases to $1.4 \times 10^{-4} \text{ M s}^{-1}$ during exercise to meet the demand of an increased metabolism rate. Assuming the Hb concentration remains the same, what must the oxygen concentration be to sustain this rate of HbO_2 formation?

- 14.83 At a certain elevated temperature, ammonia decomposes on the surface of tungsten metal as follows: $2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2$. From the following plot of the rate of the reaction versus the pressure of NH_3 , propose a mechanism for the reaction.



- 14.84 The rate of a reaction was followed by measuring the absorption of light by the reactants and products as a function of wavelength ($\lambda_1, \lambda_2, \lambda_3$) as time progressed (see Figure on p. 771). Which of the following mechanisms is consistent with the experimental data?

- (a) $\text{A} \longrightarrow \text{B}$, $\text{A} \longrightarrow \text{C}$
- (b) $\text{A} \longrightarrow \text{B} + \text{C}$
- (c) $\text{A} \longrightarrow \text{B}$, $\text{B} \longrightarrow \text{C} + \text{D}$
- (d) $\text{A} \longrightarrow \text{B}$, $\text{B} \longrightarrow \text{C}$



- 14.85 The following expression shows the dependence of the half-life ($t_{\frac{1}{2}}$) of a reaction

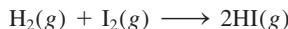


on the initial reactant concentration, $[A]_0$:

$$t_{\frac{1}{2}} \propto \frac{1}{[A]_0^{n-1}}$$

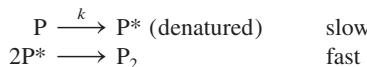
where n is the order of the reaction. (a) Derive this result. (b) Verify this result for zeroth-, first-, and second-order reactions.

- 14.86 The rate constant for the gaseous reaction



is $2.42 \times 10^{-2} M^{-1} s^{-1}$ at $400^\circ C$. Initially an equimolar sample of H_2 and I_2 is placed in a vessel at $400^\circ C$ and the total pressure is 1658 mmHg. (a) What is the initial rate ($M \text{ min}^{-1}$) of formation of HI ? (b) What are the rate of formation of HI and the concentration of HI (in molarity) after 10.0 min.

- 14.87 A protein molecule, P, of molar mass \mathcal{M} dimerizes when it is allowed to stand in solution at room temperature. A plausible mechanism is that the protein molecule is first denatured (i.e., loses its activity due to a change in overall structure) before it dimerizes:



where the asterisk denotes a denatured protein molecule. Derive an expression for the average molar mass (of P and P_2), $\bar{\mathcal{M}}$, in terms of the initial protein concentration, $[P]_0$; the concentration at time t , $[P]_t$; and \mathcal{M} . Describe how you would determine k from molar mass experiments.

Answers to Practice Exercises

14.1 (a) $0.013 M \text{ s}^{-1}$, (b) $0.013 M \text{ s}^{-1}$ (c) $-0.052 M \text{ s}^{-1}$

14.2 rate = $k[S_2O_8^{2-}][I^-]$; $k = 8.1 \times 10^{-2} M^{-1} \text{ s}^{-1}$.

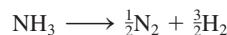
14.3 (a) 66 s. (b) 29 s. **14.4** First order; $k = 1.4 \times 10^{-2} \text{ min}^{-1}$

14.5 $1.2 \times 10^3 \text{ s}$ **14.6** (a) 3.2 min, (b) 2.1 min

14.7 240 kJ mol^{-1} **14.8** $k = 3.13 \times 10^{-9} \text{ s}^{-1}$

- 14.88** When the concentration of A in the reaction $A \longrightarrow B$ was changed from $1.20 M$ to $0.60 M$, the half-life increased from 2.0 min to 4.0 min at $25^\circ C$. Calculate the order of the reaction and the rate constant. (Hint: Use the equation in Problem 14.85.)

- 14.89** At a certain elevated temperature, ammonia decomposes on the surface of tungsten metal as follows:

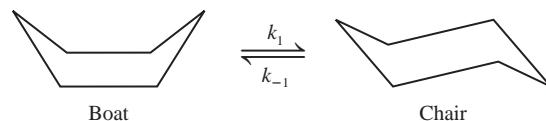


The kinetics data are expressed as the variation of the half-life with the initial pressure of NH_3 :

| P (mmHg) | 264 | 130 | 59 | 16 |
|----------------------|-----|-----|-----|----|
| $t_{\frac{1}{2}}(s)$ | 456 | 228 | 102 | 60 |

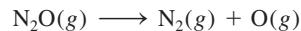
(a) Determine the order of the reaction. (b) How does the order depend on the initial pressure? (c) How does the mechanism of the reaction vary with pressure. (Hint: Use the equation in Problem 14.85.)

- 14.90** The “boat” form and “chair” form of cyclohexane (C_6H_{12}) interconvert as shown here:



In this representation, the H atoms are omitted and a C atom is assumed to be at each intersection of two lines (bonds). The conversion is first order in each direction. The activation energy for the chair to boat conversion is 41 kJ mol^{-1} . If the frequency factor is $1.0 \times 10^{12} \text{ s}^{-1}$, what is k_1 at 298 K ? The equilibrium constant K_c for the reaction is 9.83×10^3 at 298 K .

- 14.91** The activation energy for the reaction



is $2.4 \times 10^2 \text{ kg mol}^{-1}$ at 600 K . Calculate the percentage of the increase in rate from 600 K to 606 K . Comment on your results.

- 14.92** Derive Equation 14.14 for a mixed second order reaction



that is first order in both A and B.

- 14.9** (a) $NO_2 + CO \longrightarrow NO + CO_2$, (b) NO_3 , (c) The first step is rate determining.

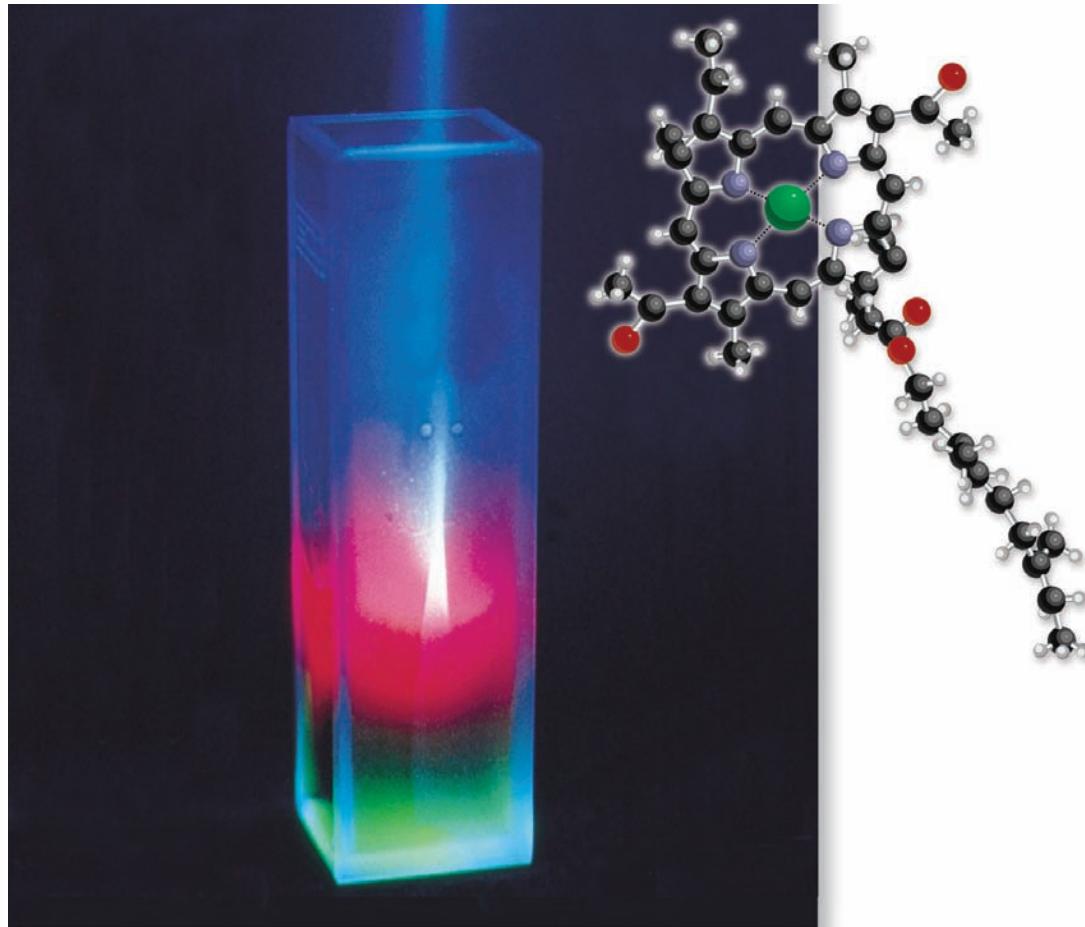
- 14.10** $k = \frac{k_1 k_2}{k_{-1}}$; an experiment to detect the presence of C could distinguish between the two proposed mechanisms.

15

Chapter

The Chemistry of Transition Metals

- 15.1 Transition Metals Have Electron Configurations with Incomplete *d* or *f* Shells 773
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In this chapter, we examine the properties of transition metal elements, that is, elements with unfilled *d* or *f* orbitals. There are about 50 transition elements, and they have widely varying and fascinating properties. To present even one interesting feature of each transition element is beyond the scope of this book. We will therefore limit our discussion to the transition elements that have incompletely filled *d* subshells and to their most commonly encountered property—the tendency to form complex ions.

15.1 | Transition Metals Have Electronic Configurations with Incomplete d or f Shells

Transition metals have incompletely filled *d* subshells or readily give rise to ions with incompletely filled *d* subshells (Figure 15.1) (The Group 2B metals—Zn, Cd, and Hg—are sometimes treated as transition metals, but they do not have this characteristic electron configuration, so they really do not belong in this category.) This attribute is responsible for several notable properties, including distinctive coloring, formation of paramagnetic compounds, catalytic activity, and especially a strong tendency to form complex ions. In this chapter, we focus on the first-row elements from scandium to copper, the most common transition metals. Table 15.1 lists some of their properties.

As we read across any period from left to right, atomic numbers increase, electrons are added to the outer shell, and the nuclear charge increases by the addition of protons. In the third-period elements—sodium to argon—the outer electrons weakly shield one another from the extra nuclear charge. Consequently, atomic radii decrease rapidly from sodium to argon, and ionization energies and electronegativities increase steadily (see Figures 2.17, 2.22, and 3.39).

For the transition metals, the trends are different. According to Table 15.1, the nuclear charge increases from scandium to copper, but electrons are being added to the inner *3d* subshell. These *3d* electrons shield the *4s* electrons from the increasing nuclear charge somewhat more effectively than outer-shell electrons can shield one another, so the atomic radii decrease less rapidly. For the same reason, electronegativities and ionization energies increase only slightly from scandium across to copper compared with the increases from sodium to argon.

Although the transition metals are less electropositive (more electronegative) than the alkali and alkaline earth metals, their standard reduction potentials suggest that all of them except copper should react with strong acids such as hydrochloric acid to produce hydrogen gas. However, most transition metals are inert toward acids or react slowly with them because of a protective layer of oxide. A case in point is chromium: Despite a rather negative standard reduction potential, it is quite inert chemically because of the formation

| 1 1A | | | | | | | | | | | | | 18 8A | | | | |
|-----------------|-----------------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|----------|----------|----------------|----------|----------|----------|
| 1 H | 2 2A | | | | | | | | | | | | | 2 He | | | |
| 3 Li | 4 Be | | | | | | | | | | | | | 5 B | | | |
| 11 Na | 12 Mg | 3 3B | 4 4B | 5 5B | 6 6B | 7 7B | 8 8B | 9 | 10 | 11 1B | 12 2B | 13 Al | 14 Si | 15 P | 16 S | 17 Cl | 18 Ar |
| 19 K | 20 Ca | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | 31 Ga | 32 Ge | 33 As | 34 Se | 35 Br | 36 Kr |
| 37 Rb | 38 Sr | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd | 49 In | 50 Sn | 51 Sb | 52 Te | 53 I | 54 Xe |
| 55 Cs | 56 Ba | 57 La | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt | 79 Au | 80 Hg | 81 Tl | 82 Pb | 83 Bi | 84 Po | 85 At | 86 Rn |
| 87 Fr | 88 Ra | 89 Ac | 104 Rf | 105 Db | 106 Sg | 107 Bh | 108 Hs | 109 Mt | 110 Ds | 111 Rg | 112 | 113 | 114 | 115 | 116 | (117) | 118 |

Figure 15.1 The transition metals (blue squares). Note that although the Group 2B elements (Zn, Cd, Hg) are described as transition metals by some chemists, neither the metals nor their ions possess incompletely filled *d* subshells.

Table 15.1 Electron Configurations and Other Properties of the First-Row Transition Metals

| | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu |
|---|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|----------------------------------|
| Electron configuration | | | | | | | | | |
| M | 4s ² 3d ¹ | 4s ² 3d ² | 4s ² 3d ³ | 4s ¹ 3d ⁵ | 4s ² 3d ⁵ | 4s ² 3d ⁶ | 4s ² 3d ⁷ | 4s ² 3d ⁸ | 4s ¹ 3d ¹⁰ |
| M ²⁺ | — | 3d ² | 3d ³ | 3d ⁴ | 3d ⁵ | 3d ⁶ | 3d ⁷ | 3d ⁸ | 3d ⁹ |
| M ³⁺ | [Ar] | 3d ¹ | 3d ² | 3d ³ | 3d ⁴ | 3d ⁵ | 3d ⁶ | 3d ⁷ | 3d ⁸ |
| Electronegativity | 1.3 | 1.5 | 1.6 | 1.6 | 1.5 | 1.8 | 1.9 | 1.9 | 1.9 |
| Ionization energy (kJ mol ⁻¹) | | | | | | | | | |
| First | 631 | 658 | 650 | 652 | 717 | 759 | 760 | 736 | 745 |
| Second | 1235 | 1309 | 1413 | 1591 | 1509 | 1561 | 1645 | 1751 | 1958 |
| Third | 2389 | 2650 | 2828 | 2986 | 3250 | 2956 | 3231 | 3393 | 3578 |
| Radius (pm) | | | | | | | | | |
| M | 162 | 147 | 134 | 130 | 135 | 126 | 125 | 124 | 128 |
| M ²⁺ | — | 90 | 88 | 85 | 80 | 77 | 75 | 69 | 72 |
| M ³⁺ | 81 | 77 | 74 | 64 | 66 | 60 | 64 | — | — |
| Standard reduction potential (V)* | -2.08 | -1.63 | -1.2 | -0.74 | -1.18 | -0.44 | -0.28 | -0.25 | 0.34 |

*The half-reaction is M²⁺ (aq) + 2e⁻ → M(s) (except for Sc and Cr, where the ions are Sc³⁺ and Cr³⁺, respectively).

on its surface of chromium(III) oxide (Cr₂O₃). Consequently, chromium is commonly used as a protective and noncorrosive plating on other metals. On automobile bumpers and trim, chromium plating serves a decorative as well as a functional purpose.

General Physical Properties

Most of the transition metals have relatively small atomic radii and a close-packed structure (see Figure 6.28) in which each atom has a coordination number of 12. The combined effect of small atomic size and close packing result in strong metallic bonds. Therefore, transition metals have higher densities, higher melting and boiling points, and higher heats of fusion and vaporization than the Group 1A, 2A, and 2B metals (Table 15.2).

Table 15.2 Physical Properties of Elements K to Zn

| | 1A | | 2A | | Transition Metals | | | | | | 2B | |
|-------------------------------|------|------|------|------|-------------------|------|------|------|------|------|------|-------|
| | K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
| Atomic radius (pm) | 235 | 197 | 162 | 147 | 134 | 130 | 135 | 126 | 125 | 124 | 128 | 138 |
| Melting Point (°C) | 63.7 | 838 | 1539 | 1668 | 1900 | 1875 | 1245 | 1536 | 1495 | 1453 | 1083 | 419.5 |
| Boiling Point (°C) | 760 | 1440 | 2730 | 3260 | 3450 | 2665 | 2150 | 3000 | 2900 | 2730 | 2595 | 906 |
| Density (g cm ⁻³) | 0.86 | 1.54 | 3.0 | 4.51 | 6.1 | 7.19 | 7.43 | 7.86 | 8.9 | 8.9 | 8.96 | 7.14 |

Electron Configurations

The electron configurations of the first-row transition metals were discussed in Section 2.2. Calcium has the electron configuration $[Ar]4s^2$. From scandium across to copper, electrons are added to the $3d$ orbitals. Thus, the outer electron configuration of scandium is $4s^23d^1$, that of titanium is $4s^23d^2$, and so on. The two exceptions are chromium and copper, whose outer electron configurations are $4s^13d^5$ and $4s^13d^{10}$, respectively. These irregularities are the result of the extra stability associated with half-filled and completely filled $3d$ subshells.

When the first-row transition metals form cations, electrons are removed first from the $4s$ orbitals and then from the $3d$ orbitals. (This is the opposite of the order in which orbitals are filled in atoms.) For example, the outer electron configuration of Fe^{2+} is $3d^6$, not $4s^23d^4$.

Oxidation States

Transition metals exhibit variable oxidation states in their compounds. Figure 15.2 shows that the common oxidation states for each element from scandium to copper include +2, +3, or both. The +3 oxidation states are more stable at the beginning of the series, whereas the +2 oxidation states are more stable toward the end. To understand this trend, you must examine the ionization energy plots in Figure 15.3. In general, the ionization energies increase gradually from left to right. However, the third ionization energy (when an electron is removed from the $3d$ orbital) increases more rapidly than the first and second ionization energies. Because it takes more energy to remove the third electron from the metals near the end of the row than from those near the beginning, the metals near the end tend to form M^{2+} ions rather than M^{3+} ions.

The highest oxidation state for a transition metal, that of manganese ($4s^23d^5$), is +7. For elements to the right of Mn (Fe to Cu), the oxidation numbers are lower. Transition metals usually exhibit their highest oxidation states in compounds with very electronegative elements such as oxygen and fluorine. Examples include V_2O_5 , CrO_3 , and Mn_2O_7 .

| Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu |
|----|----|----|----|----|----|----|----|----|
| | | | | +7 | | | | |
| | | | | +6 | +6 | +6 | | |
| | | | +5 | +5 | +5 | +5 | | |
| | +4 | +4 | +4 | +4 | +4 | +4 | | |
| +3 | +3 | +3 | +3 | +3 | +3 | +3 | +3 | +3 |
| | +2 | +2 | +2 | +2 | +2 | +2 | +2 | +2 |
| | | | | | | | | +1 |

Figure 15.2 Oxidation states of the first-row transition metals. The most stable oxidation numbers are shown in color. The zero oxidation state is encountered in some compounds, such as $Ni(CO)_4$ and $Fe(CO)_5$.