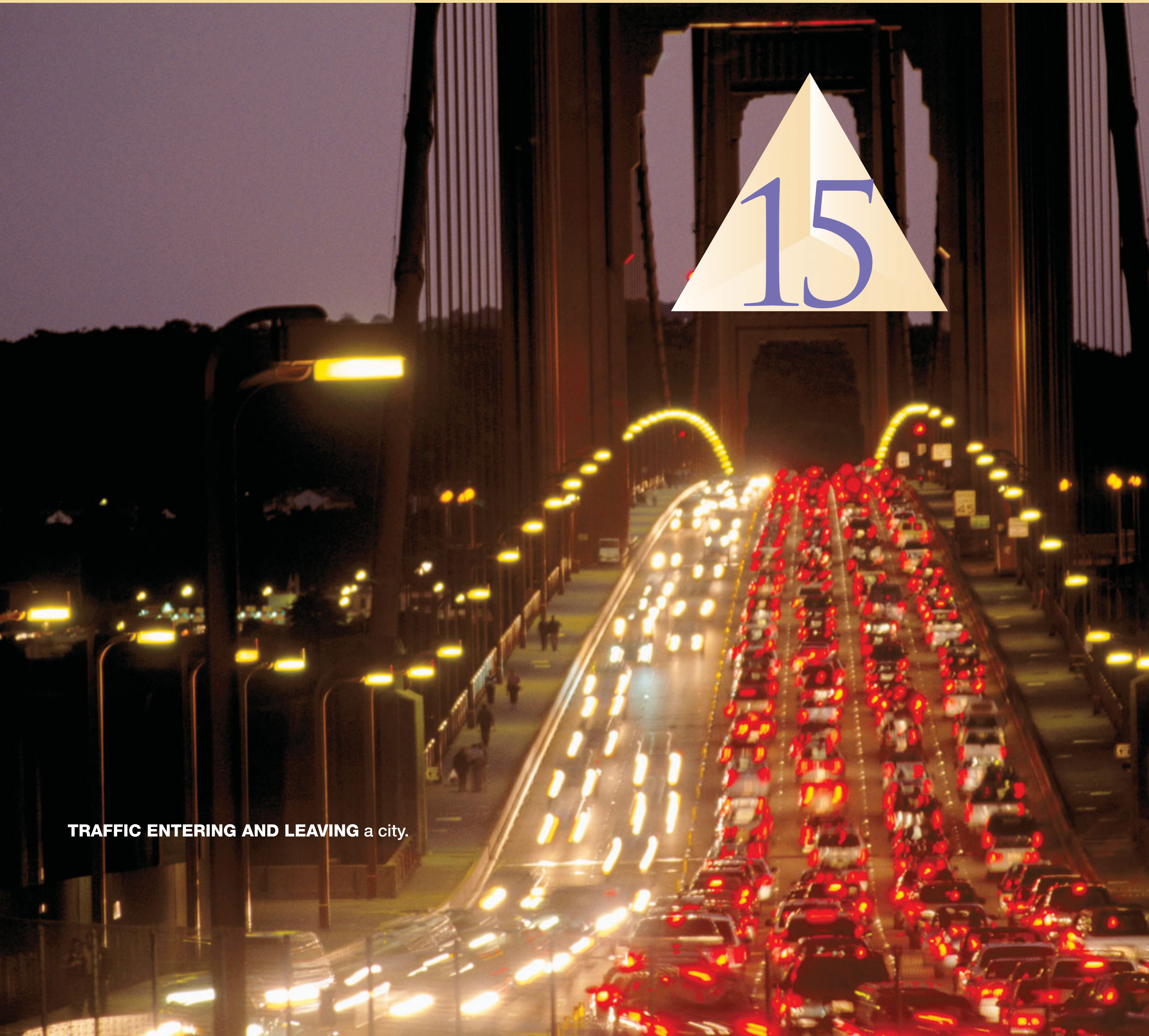
WHAT'S AHEAD

15.1 THE CONCEPT OF EQUILIBRIUM
We begin by examining reversible reactions and the concept of equilibrium.

15.2 THE EQUILIBRIUM CONSTANT
We define the *equilibrium constant* based on rates of forward and reverse reactions, and learn how to write *equilibrium-constant expressions* for homogeneous reactions.

15.3 UNDERSTANDING AND WORKING WITH EQUILIBRIUM CONSTANTS
We learn to interpret the magnitude of an equilibrium constant and how its value depends on the way the corresponding chemical equation is expressed.

15.4 HETEROGENEOUS EQUILIBRIA
We then learn how to write equilibrium-constant expressions for heterogeneous reactions.



TRAFFIC ENTERING AND LEAVING a city.

15.5 CALCULATING EQUILIBRIUM CONSTANTS
We see that the value of an equilibrium constant can be calculated from equilibrium concentrations of reactants and products.

15.6 APPLICATIONS OF EQUILIBRIUM CONSTANTS
We also see that equilibrium constants can be used to predict equilibrium concentrations of reactants and products and to determine the direction in which a reaction mixture must proceed to achieve equilibrium.

15.7 LE CHÂTELIER'S PRINCIPLE
We discuss *Le Châtelier's principle*, which predicts how a system at equilibrium responds to changes in concentration, volume, pressure, and temperature.

CHEMICAL EQUILIBRIUM

TO BE IN EQUILIBRIUM IS to be in a state of balance. A tug of war in which the two sides pull with equal force so that the rope does not move is an example of a *static* equilibrium, one in which an object is at rest. Equilibria can also be *dynamic*, as illustrated in the chapter-opening photograph, which shows cars traveling in both directions over a bridge that serves as the entry to a city. If the rate at which cars leave the city equals the rate at which they enter, the two opposing processes are in balance, and the net number of cars in the city is constant.

We have already encountered several instances of dynamic equilibrium. For example, the vapor above a liquid in a closed container is in equilibrium with the liquid phase (Section 11.5), which means that the rate at which molecules escape from the liquid into the gas phase equals the rate at which molecules in the gas phase become part of the liquid. Similarly, in a saturated sodium chloride solution in contact with undissolved sodium chloride, the solid is in equilibrium with the ions dispersed in water. (Section 13.2) The rate at which ions leave the solid surface equals the rate at which other ions leave the liquid and become part of the solid.

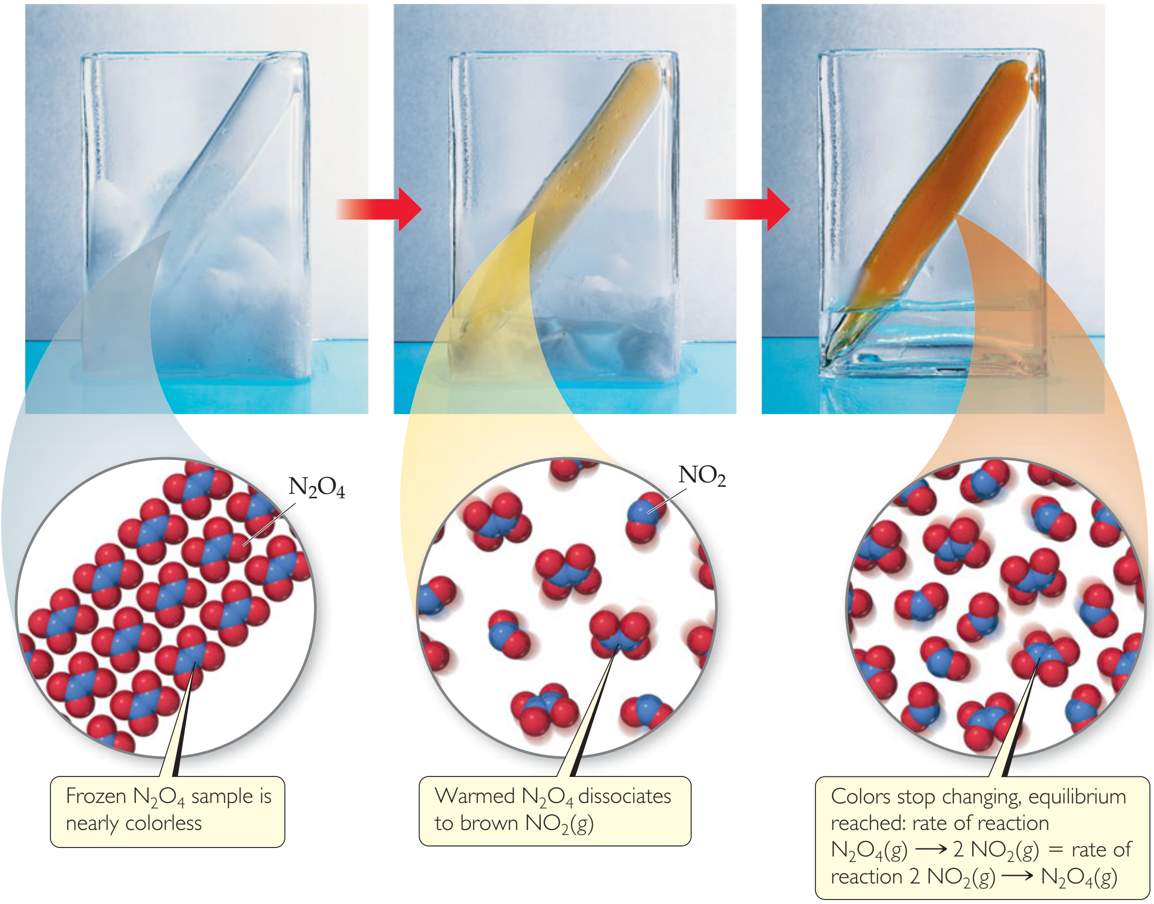
In this chapter we consider dynamic equilibria in chemical reactions. **Chemical equilibrium** *occurs when opposing reactions proceed at equal rates*: The rate at which the products form from the reactants equals the rate at which the reactants form from the products. As a result, concentrations cease to change, making the reaction appear to be stopped. Chemical equilibria are involved in many natural phenomena and play important roles in many industrial processes. In this and the next two chapters, we will explore chemical equilibrium in some detail. Later, in Chapter 19, we will learn how to relate chemical equilibria to thermodynamics. Here we learn how to express the equilibrium state of a reaction in quantitative terms and study the factors that determine the relative concentrations of reactants and products in equilibrium mixtures.

15.1 THE CONCEPT OF EQUILIBRIUM

Let's examine a simple chemical reaction to see how it reaches an *equilibrium state*—a mixture of reactants and products whose concentrations no longer change with time. We begin with N_2O_4, a colorless substance that dissociates to form brown NO_2. ▼ **FIGURE 15.1** shows a sample of frozen N_2O_4 inside a sealed tube. The solid N_2O_4 vaporizes as it is warmed above its boiling point (21.2 °C), and the gas turns darker as the colorless N_2O_4 gas dissociates into brown NO_2 gas. Eventually, even though there is still N_2O_4 in the tube, the color stops getting darker because the system reaches equilibrium. We are left with an *equilibrium mixture* of N_2O_4 and NO_2 in which the concentrations of the gases no longer change as time passes. Because the reaction is in a closed system, where no gases can escape, equilibrium will eventually be reached.

GO FIGURE

How can you tell if you are at equilibrium?



▲ **FIGURE 15.1 The equilibrium between NO_2 and N_2O_4.**

The equilibrium mixture results because the reaction is *reversible*: N_2O_4 can form NO_2, and NO_2 can form N_2O_4. This situation is represented by writing the equation for the reaction with two half arrows pointing in opposite directions: (Section 4.1)

$$\underset{\text{Colorless}}{N_2O_4(g)} \rightleftharpoons \underset{\text{Brown}}{2\,NO_2(g)} \qquad [15.1]$$

We can analyze this equilibrium using our knowledge of kinetics. Let's call the decomposition of N_2O_4 the forward reaction and the formation of N_2O_4 the reverse reaction. In this case, both the forward reaction and the reverse reaction are elementary reactions. As we learned in Section 14.6, the rate laws for elementary reactions can be written from their chemical equations:

$$\textit{Forward reaction:}\quad N_2O_4(g) \longrightarrow 2\,NO_2(g) \qquad \text{Rate}_f = k_f[N_2O_4] \qquad [15.2]$$

$$\textit{Reverse reaction:}\quad 2\,NO_2(g) \longrightarrow N_2O_4(g) \qquad \text{Rate}_r = k_r[NO_2]^2 \qquad [15.3]$$

At equilibrium, the rate at which NO_2 forms in the forward reaction equals the rate at which N_2O_4 forms in the reverse reaction:

$$\underset{\text{Forward reaction}}{k_f[N_2O_4]} = \underset{\text{Reverse reaction}}{k_r[NO_2]^2} \qquad [15.4]$$

Rearranging this equation gives

$$\frac{[NO_2]^2}{[N_2O_4]} = \frac{k_f}{k_r} = \text{a constant} \qquad [15.5]$$

From Equation 15.5 we see that the quotient of two rate constants is another constant. We also see that, at equilibrium, the ratio of the concentration terms equals this same constant. (We consider this constant, called the equilibrium constant, in Section 15.2.) It makes no difference whether we start with N_2O_4 or with NO_2, or even with some mixture of the two. At equilibrium, at a given temperature, the ratio equals a specific value. Thus, there is an important constraint on the proportions of N_2O_4 and NO_2 at equilibrium.

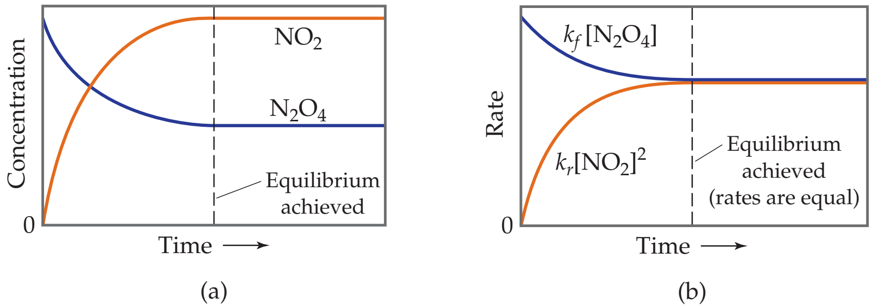
Once equilibrium is established, the concentrations of N_2O_4 and NO_2 no longer change, as shown in ▼ **FIGURE 15.2**(a). However, the fact that the composition of the equilibrium mixture remains constant with time does not mean that N_2O_4 and NO_2 stop reacting. On the contrary, the equilibrium is *dynamic*—which means some N_2O_4 is always converting to NO_2 and some NO_2 is always converting to N_2O_4. At equilibrium, however, the two processes occur at the same rate, as shown in Figure 15.2(b).

We learn several important lessons about equilibrium from this example:

- At equilibrium, the concentrations of reactants and products no longer change with time.
- For equilibrium to occur, neither reactants nor products can escape from the system.
- At equilibrium, a particular ratio of concentration terms equals a constant.

GO FIGURE

At equilibrium, are the concentrations of NO_2 and N_2O_4 equal?



◀ **FIGURE 15.2 Achieving chemical equilibrium in the $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ reaction.** Equilibrium occurs when the rate of the forward reaction equals the rate of the reverse reaction.

GIVE IT SOME THOUGHT

a. Which quantities are equal in a dynamic equilibrium?
b. If the rate constant for the forward reaction in Equation 15.1 is larger than the rate constant for the reverse reaction, will the constant in Equation 15.5 be greater than 1 or smaller than 1?

15.2 | THE EQUILIBRIUM CONSTANT

A reaction in which reactants convert to products and products convert to reactants in the same reaction vessel naturally leads to an equilibrium, regardless of how complicated the reaction is and regardless of the nature of the kinetic processes for the forward and reverse reactions. Consider the synthesis of ammonia from nitrogen and hydrogen:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad [15.6]$$

This reaction is the basis for the **Haber process**, which is critical for the production of fertilizers and therefore critical to the world's food supply. In the Haber process, N_2 and H_2 react at high pressure and temperature in the presence of a catalyst to form ammonia. In a closed system, however, the reaction does not lead to complete consumption of the N_2 and H_2. Rather, at some point the reaction appears to stop with all three components of the reaction mixture present at the same time.

How the concentrations of H_2, N_2, and NH_3 vary with time is shown in ▼ **FIGURE 15.3**. Notice that an equilibrium mixture is obtained regardless of whether we begin with N_2 and H_2 or with NH_3. *The equilibrium condition is reached from either direction.*

GIVE IT SOME THOUGHT

How do we know when equilibrium has been reached in a chemical reaction?

An expression similar to Equation 15.5 governs the concentrations of N_2, H_2, and NH_3 at equilibrium. If we were to systematically change the relative amounts of the three gases in the starting mixture and then analyze each equilibrium mixture, we could determine the relationship among the equilibrium concentrations.

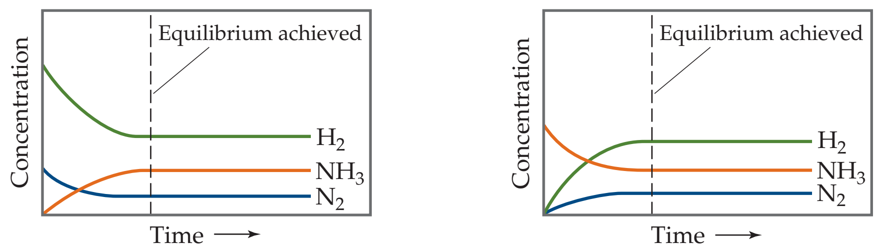
Chemists carried out studies of this kind on other chemical systems in the nineteenth century before Haber's work. In 1864, Cato Maximilian Guldberg (1836–1902) and Peter Waage (1833–1900) postulated their **law of mass action**, which expresses, for any reaction, the relationship between the concentrations of the reactants and products present at equilibrium. Suppose we have the general equilibrium equation

$$a\,A + b\,B \rightleftharpoons d\,D + e\,E \qquad [15.7]$$

where A, B, D, and E are the chemical species involved and a, b, d, and e are their coefficients in the balanced chemical equation. According to the law of mass action, the equilibrium condition is described by the expression

$$K_c = \frac{[D]^d[E]^e \;\longleftarrow \text{products}}{[A]^a[B]^b \;\longleftarrow \text{reactants}} \qquad [15.8]$$

We call this relationship the **equilibrium-constant expression** (or merely the *equilibrium expression*) for the reaction. The constant K_c, the **equilibrium constant**, is the numerical value obtained when we substitute molar equilibrium concentrations



► **FIGURE 15.3 The same equilibrium is reached whether we start with only reactants (N_2 and H_2) or with only product (NH_3).**

CHEMISTRY PUT TO WORK

The Haber Process

The quantity of food required to feed the ever-increasing human population far exceeds that provided by nitrogen-fixing plants. (Section 14.7) Therefore, human agriculture requires substantial amounts of ammonia-based fertilizers for croplands. Of all the chemical reactions that humans have learned to control for their own purposes, the synthesis of ammonia from hydrogen and atmospheric nitrogen is one of the most important.

In 1912 the German chemist Fritz Haber (1868–1934) developed the Haber process (Equation 15.6). The process is sometimes also called the *Haber–Bosch process* to honor Karl Bosch, the engineer who developed the industrial process on a large scale. The engineering needed to implement the Haber process requires the use of temperatures and pressures (approximately 500 °C and 200 to 600 atm) that were difficult to achieve at that time.

The Haber process provides a historically interesting example of the complex impact of chemistry on our lives. At the start of World War I, in 1914, Germany depended on nitrate deposits in Chile for the nitrogen-containing compounds needed to manufacture explosives. During the war, the Allied naval blockade of South America cut off this supply. However, by using the Haber reaction to fix nitrogen from air, Germany was able to continue to produce explosives. Experts have estimated that World War I would have ended before 1918 had it not been for the Haber process.

From these unhappy beginnings as a major factor in international warfare, the Haber process has become the world's principal source of fixed nitrogen. The same process that prolonged World War I has enabled the manufacture of fertilizers that have increased crop yields, thereby saving millions of people from starvation. About 40 billion pounds of ammonia are manufactured annually in the United States, mostly by the Haber process. The ammonia can be applied directly to the soil (▼ **FIGURE 15.4**), or it can be converted into ammonium salts that are also used as fertilizers.

Haber was a patriotic German who gave enthusiastic support to his nation's war effort. He served as chief of Germany's Chemical Warfare Service during World War I and developed the use of chlorine as a poison-gas weapon. Consequently, the decision to award him the Nobel Prize in Chemistry in 1918 was the subject of considerable controversy and criticism. The ultimate irony, however, came in 1933 when Haber was expelled from Germany because he was Jewish.

RELATED EXERCISES: 15.46 and 15.76

◀ **FIGURE 15.4 Liquid ammonia used as fertilizer by direct injection into soil.**

into the equilibrium-constant expression. The subscript c on the K indicates that concentrations expressed in molarity are used to evaluate the constant.

The numerator of the equilibrium-constant expression is the product of the concentrations of all substances on the product side of the equilibrium equation, each raised to a power equal to its coefficient in the balanced equation. The denominator is similarly derived from the reactant side of the equilibrium equation. Thus, for the Haber process, $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, the equilibrium-constant expression is

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \qquad [15.9]$$

Once we know the balanced chemical equation for a reaction that reaches equilibrium, we can write the equilibrium-constant expression even if we do not know the reaction mechanism. *The equilibrium-constant expression depends only on the stoichiometry of the reaction, not on its mechanism.*

The value of the equilibrium constant at any given temperature does not depend on the initial amounts of reactants and products. It also does not matter whether other substances are present, as long as they do not react with a reactant or a product. The value of K_c depends only on the particular reaction and on the temperature.

SAMPLE EXERCISE 15.1 Writing Equilibrium-Constant Expressions

Write the equilibrium expression for K_c for the following reactions:

(a) $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$

(b) $2\,NO(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$

(c) $Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^+(aq)$

SOLUTION

Analyze We are given three equations and are asked to write an equilibrium-constant expression for each.

Plan Using the law of mass action, we write each expression as a quotient having the product concentration terms in the numerator and the reactant concentration terms in the denominator. Each concentration term is raised to the power of its coefficient in the balanced chemical equation.

Solve

(a) $K_c = \dfrac{[O_2]^3}{[O_3]^2}$ **(b)** $K_c = \dfrac{[NOCl]^2}{[NO]^2[Cl_2]}$ **(c)** $K_c = \dfrac{[Ag(NH_3)_2{}^+]}{[Ag^+][NH_3]^2}$

PRACTICE EXERCISE

Write the equilibrium-constant expression K_c for **(a)** $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, **(b)** $Cd^{2+}(aq) + 4\,Br^-(aq) \rightleftharpoons CdBr_4{}^{2-}(aq)$.

Answers: **(a)** $K_c = \dfrac{[HI]^2}{[H_2][I_2]}$ **(b)** $K_c = \dfrac{[CdBr_4{}^{2-}]}{[Cd^{2+}][Br^-]^4}$

Evaluating K_c

We can illustrate how the law of mass action was discovered empirically and demonstrate that the equilibrium constant is independent of starting concentrations by examining a series of experiments involving dinitrogen tetroxide and nitrogen dioxide:

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \qquad K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad [15.10]$$

We start with several sealed tubes containing different concentrations of NO_2 and N_2O_4. The tubes are kept at 100 °C until equilibrium is reached. We then analyze the mixtures and determine the equilibrium concentrations of NO_2 and N_2O_4, which are shown in ▼ TABLE 15.1.

To evaluate K_c, we insert the equilibrium concentrations into the equilibrium-constant expression. For example, using Experiment 1 data, $[NO_2] = 0.0172\,M$ and $[N_2O_4] = 0.00140\,M$, we find

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{[0.0172]^2}{0.00140} = 0.211$$

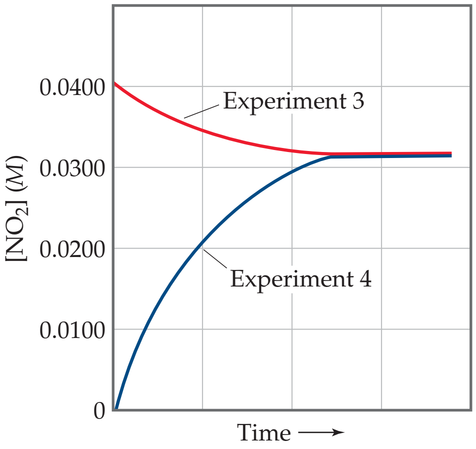
TABLE 15.1 • Initial and Equilibrium Concentrations of $N_2O_4(g)$ and $NO_2(g)$ at 100 °C

Experiment	Initial $[N_2O_4]$ (M)	Initial $[NO_2]$ (M)	Equilibrium $[N_2O_4]$ (M)	Equilibrium $[NO_2]$ (M)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

Proceeding in the same way, the values of K_c for the other samples are calculated. Note from Table 15.1 that the value for K_c is constant (within the limits of experimental error) even though the initial concentrations vary. Furthermore, Experiment 4 shows that equilibrium can be achieved beginning with N_2O_4 rather than with NO_2. That is, equilibrium can be approached from either direction. ▶ **FIGURE 15.5** shows how Experiments 3 and 4 result in the same equilibrium mixture even though the two experiments start with very different NO_2 concentrations.

Notice that no units are given for K_c either in Table 15.1 or in the calculation we just did using Experiment 1 data. It is common practice to write equilibrium constants without units for reasons that we address later in this section.

Recall that we began our discussion of equilibrium in terms of rates. Equation 15.5 shows that K_c is equal to k_f/k_r, the ratio of the forward rate constant to the reverse rate constant. For the N_2O_4/NO_2 reaction, $K_c = 0.212$, which means that k_r is 4.72 times as large as k_f (since $1/0.212 = 4.72$). It is not possible to obtain the absolute value of either rate constant knowing only the value of K_c.



▲ **FIGURE 15.5 The same equilibrium mixture is produced regardless of the initial NO_2 concentration.** The concentration of NO_2 either increases or decreases until equilibrium is reached.

GIVE IT SOME THOUGHT

How does the value of K_c in Equation 15.10 depend on the starting concentrations of NO_2 and N_2O_4?

Equilibrium Constants in Terms of Pressure, K_p

When the reactants and products in a chemical reaction are gases, we can formulate the equilibrium-constant expression in terms of partial pressures. When partial pressures in atmospheres are used in the expression, we denote the equilibrium constant K_p (where the subscript p stands for pressure). For the general reaction in Equation 15.7, we have

$$K_p = \frac{(P_D)^d(P_E)^e}{(P_A)^a(P_B)^b} \qquad [15.11]$$

where P_A is the partial pressure of A in atmospheres, P_B is the partial pressure of B in atmospheres, and so forth. For example, for our N_2O_4/NO_2 reaction we have

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}}$$

GIVE IT SOME THOUGHT

What is the difference between the equilibrium constant K_c and the equilibrium constant K_p?

For a given reaction, the numerical value of K_c is generally different from the numerical value of K_p. We must therefore take care to indicate, via subscript c or p, which constant we are using. It is possible, however, to calculate one from the other using the ideal-gas equation: (Section 10.4)

$$PV = nRT, \text{ so } P = \frac{n}{V}RT \qquad [15.12]$$

The usual units for n/V are mol/L, which equals molarity, M. For substance A in our generic reaction, we therefore see that

$$P_A = \frac{n_A}{V}RT = [A]RT \qquad [15.13]$$

When we substitute Equation 15.13 and like expressions for the other gaseous components of the reaction into Equation 15.11, we obtain a general expression relating K_p and K_c:

$$K_p = K_c(RT)^{\Delta n} \qquad [15.14]$$

The quantity Δn is the change in the number of moles of gas in the balanced chemical equation. It equals the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants:

$$\Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant}) \qquad [15.15]$$

For example, in the $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ reaction, there are two moles of product NO_2 and one mole of reactant N_2O_4. Therefore, $\Delta n = 2 - 1 = 1$, and $K_p = K_c(RT)$ for this reaction.

From Equation 15.14, we see that $K_p = K_c$ only when the same number of moles of gas appears on both sides of the balanced chemical equation, so that $\Delta n = 0$.

SAMPLE EXERCISE 15.2 Converting between K_c and K_p

For the Haber process,

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

$K_c = 9.60$ at 300 °C. Calculate K_p for this reaction at this temperature.

SOLUTION

Analyze We are given K_c for a reaction and asked to calculate K_p.

Plan The relationship between K_c and K_p is given by Equation 15.14. To apply that equation, we must determine Δn by comparing the number of moles of product with the number of moles of reactants (Equation 15.15).

Solve With 2 mol of gaseous products ($2\,NH_3$) and 4 mol of gaseous reactants ($1\,N_2 + 3\,H_2$), $\Delta n = 2 - 4 = -2$. (Remember that Δ functions are always based on *products minus reactants*.) The temperature is $273 + 300 = 573$ K. The value for the ideal-gas constant, R, is 0.08206 L-atm/mol-K. Using $K_c = 9.60$, we therefore have

$$K_p = K_c(RT)^{\Delta n} = (9.60)(0.08206 \times 573)^{-2} = \frac{(9.60)}{(0.08206 \times 573)^2} = 4.34 \times 10^{-3}$$

PRACTICE EXERCISE

For the equilibrium $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$, K_c is 4.08×10^{-3} at 1000 K. Calculate the value for K_p.

Answer: 0.335

Equilibrium Constants and Units

You may wonder why equilibrium constants are reported without units. The equilibrium constant is related to the kinetics of a reaction as well as to the thermodynamics. (We explore this latter connection in Chapter 19.) Equilibrium constants derived from thermodynamic measurements are defined in terms of *activities* rather than concentrations or partial pressures.

The activity of any substance in an *ideal* mixture is the ratio of the concentration or pressure of the substance either to a reference concentration (1 M) or to a reference pressure (1 atm). For example, if the concentration of a substance in an equilibrium mixture is 0.010 M, its activity is $0.010\,M/1\,M = 0.010$. The units of such ratios always cancel and, consequently, activities have no units. Furthermore, the numerical value of the activity equals the concentration. For pure solids and pure liquids, the situation is even simpler because the activities then merely equal 1 (again with no units).

In real systems, activities are also ratios that have no units. Even though these activities may not be exactly numerically equal to concentrations, we will ignore the differences. All we need to know at this point is that activities have no units. As a result, the *thermodynamic equilibrium constants* derived from them also have no units. It is therefore common practice to write all types of equilibrium constants without units, a practice that we adhere to in this text. In more advanced chemistry courses, you may make more rigorous distinctions between concentrations and activities.

GIVE IT SOME THOUGHT

If the concentration of N_2O_4 in an equilibrium mixture is 0.00140 M, what is its activity? (Assume the solution is ideal.)

15.3 UNDERSTANDING AND WORKING WITH EQUILIBRIUM CONSTANTS

Before doing calculations with equilibrium constants, it is valuable to understand what the magnitude of an equilibrium constant can tell us about the relative concentrations of reactants and products in an equilibrium mixture. It is also useful to consider how the magnitude of any equilibrium constant depends on how the chemical equation is expressed.

The Magnitude of Equilibrium Constants

The magnitude of the equilibrium constant for a reaction gives us important information about the composition of the equilibrium mixture. For example, consider the experimental data for the reaction of carbon monoxide gas and chlorine gas at 100 °C to form phosgene ($COCl_2$), a toxic gas used in the manufacture of certain polymers and insecticides:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad K_c = \frac{[COCl_2]}{[CO][Cl_2]} = 4.56 \times 10^9$$

For the equilibrium constant to be so large, the numerator of the equilibrium-constant expression must be approximately a billion (10^9) times larger than the denominator. Thus, the equilibrium concentration of $COCl_2$ must be much greater than that of CO or Cl_2, and in fact this is just what we find experimentally. We say that this equilibrium *lies to the right* (that is, toward the product side). Likewise, a very small equilibrium constant indicates that the equilibrium mixture contains mostly reactants. We then say that the equilibrium *lies to the left*. In general,

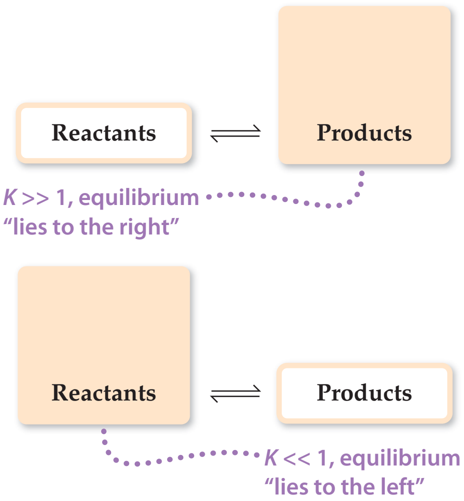
If $K \gg 1$ *(large K):* Equilibrium lies to right, products predominate

If $K \ll 1$ *(small K):* Equilibrium lies to left, reactants predominate

These situations are summarized in ▶ **FIGURE 15.6**. Remember, it is forward and reverse *rates* that are equal at equilibrium, not concentrations.

GO FIGURE

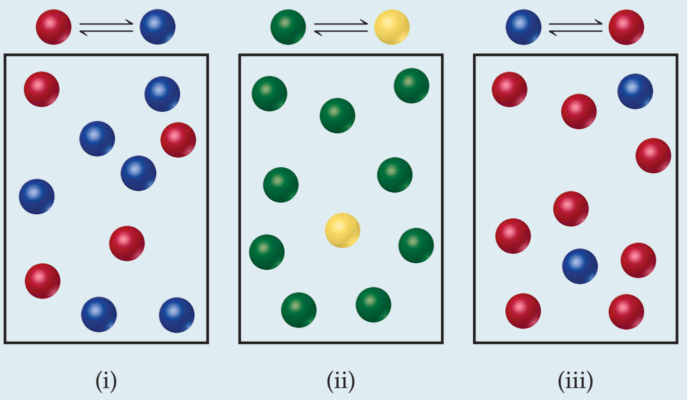
What would this figure look like for a reaction in which $K \approx 1$?



▲ **FIGURE 15.6 Relationship between magnitude of K and composition of an equilibrium mixture.**

SAMPLE EXERCISE 15.3 Interpreting the Magnitude of an Equilibrium Constant

The following diagrams represent three systems at equilibrium, all in the same-size containers. **(a)** Without doing any calculations, rank the systems in order of increasing K_c. **(b)** If the volume of the containers is 1.0 L and each sphere represents 0.10 mol, calculate K_c for each system.



SOLUTION

Analyze We are asked to judge the relative magnitudes of three equilibrium constants and then to calculate them.

Plan (**a**) The more product present at equilibrium, relative to reactant, the larger the equilibrium constant. (**b**) The equilibrium constant is given by Equation 15.8.

Solve

(**a**) Each box contains 10 spheres. The amount of product in each varies as follows: (i) 6, (ii) 1, (iii) 8. Therefore, the equilibrium constant varies in the order (ii) < (i) < (iii), from smallest (most reactant) to largest (most products).

(**b**) In (i) we have 0.60 mol/L product and 0.40 mol/L reactant, giving $K_c = 0.60/0.40 = 1.5$. (You will get the same result by merely dividing the number of spheres of each kind: 6 spheres/4 spheres = 1.5.) In (ii) we have 0.10 mol/L product and 0.90 mol/L reactant, giving $K_c = 0.10/0.90 = 0.11$ (or 1 sphere/9 spheres = 0.11). In (iii) we have 0.80 mol/L product and 0.20 mol/L reactant, giving $K_c = 0.80/0.20 = 4.0$ (or 8 spheres/2 spheres = 4.0). These calculations verify the order in (a).

Comment Imagine a drawing that represents a reaction with a very small or very large value of K_c. For example, what would the drawing look like if $K_c = 1 \times 10^{-5}$? In that case there would need to be 100,000 reactant molecules for only 1 product molecule. But then, that would be impractical to draw.

PRACTICE EXERCISE

For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, $K_p = 794$ at 298 K and $K_p = 55$ at 700 K. Is the formation of HI favored more at the higher or lower temperature?

Answer: at the lower temperature because K_p is larger at the lower temperature

The Direction of the Chemical Equation and *K*

We have seen that we can represent the N_2O_4/NO_2 equilibrium as

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \quad K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \quad (\text{at } 100\ ^\circ\text{C}) \qquad [15.16]$$

We could equally well consider this equilibrium in terms of the reverse reaction:

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g)$$

The equilibrium expression is then

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{0.212} = 4.72 \quad (\text{at } 100\ ^\circ\text{C}) \qquad [15.17]$$

Equation 15.17 is the reciprocal of the expression in Equation 15.16. *The equilibrium-constant expression for a reaction written in one direction is the reciprocal of the expression for the reaction written in the reverse direction*. Consequently, the numerical value of the equilibrium constant for the reaction written in one direction is the reciprocal of that for the reverse reaction. Both expressions are equally valid, but it is meaningless to say that the equilibrium constant for the equilibrium between NO_2 and N_2O_4 is “0.212” or “4.72” unless we indicate how the equilibrium reaction is written and specify the temperature. Therefore, whenever you are using an equilibrium constant, you should always write the associated balanced chemical equation.

SAMPLE EXERCISE 15.4 **Evaluating an Equilibrium Constant When an Equation Is Reversed**

For the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$$

that is run at 25 °C, $K_c = 1 \times 10^{-30}$. Use this information to write the equilibrium-constant expression and calculate the equilibrium constant for the reaction

$$2\,NO(g) \rightleftharpoons N_2(g) + O_2(g)$$

SOLUTION

Analyze We are asked to write the equilibrium-constant expression for a reaction and to determine the value of K_c given the chemical equation and equilibrium constant for the reverse reaction.

Plan The equilibrium-constant expression is a quotient of products over reactants, each raised to a power equal to its coefficient in the balanced equation. The value of the equilibrium constant is the reciprocal of that for the reverse reaction.

Solve

Writing products over reactants, we have

$$K_c = \frac{[N_2][O_2]}{[NO]^2}$$

Both the equilibrium-constant expression and the numerical value of the equilibrium constant are the reciprocals of those for the formation of NO from N_2 and O_2:

$$K_c = \frac{[N_2][O_2]}{[NO]^2} = \frac{1}{1 \times 10^{-30}} = 1 \times 10^{30}$$

Comment Regardless of the way we express the equilibrium among NO, N_2, and O_2, at 25 °C it lies on the side that favors N_2 and O_2. Thus, the equilibrium mixture will contain mostly N_2 and O_2 with very little NO present.

PRACTICE EXERCISE

For $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, $K_p = 4.34 \times 10^{-3}$ at 300 °C. What is the value of K_p for the reverse reaction?

Answer: 2.30×10^2

Relating Chemical Equation Stoichiometry and Equilibrium Constants

There are many ways to write a balanced chemical equation for a given reaction. For example, if we multiply Equation 15.1, $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$ by 2, we have

$$2\,N_2O_4(g) \rightleftharpoons 4\,NO_2(g)$$

This chemical equation is balanced and might be written this way in some contexts. Therefore, the equilibrium-constant expression for this equation is

$$K_c = \frac{[NO_2]^4}{[N_2O_4]^2}$$

which is the square of the equilibrium-constant expression given in Equation 15.10 for the reaction as written in Equation 15.1: $[NO_2]^2/[N_2O_4]$. Because the new equilibrium-constant expression equals the original expression squared, the new equilibrium constant K_c equals the original constant squared: $0.212^2 = 0.0449$ (at 100 °C). Once again, it is important to remember that you must relate each equilibrium constant you work with to a *specific* balanced chemical equation. The concentrations of the substances in the equilibrium mixture will be the same no matter how you write the chemical equation, but the value of K_c you calculate depends completely on how you write the reaction.

GIVE IT SOME THOUGHT

How does the magnitude of K_p for the reaction $2\,HI(g) \rightleftharpoons H_2(g) + I_2(g)$ change if the equilibrium is written $6\,HI(g) \rightleftharpoons 3\,H_2(g) + 3\,I_2(g)$?

It is also possible to calculate the equilibrium constant for a reaction if we know the equilibrium constants for other reactions that add up to give us the one we want, similar to Hess's law. (Section 5.6) For example, consider the following two reactions, their equilibrium-constant expressions, and their equilibrium constants at 100 °C:

1. $2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g) \quad K_c = \dfrac{[NO]^2[Br_2]}{[NOBr]^2} = 0.014$

2. $Br_2(g) + Cl_2(g) \rightleftharpoons 2\,BrCl(g) \quad K_c = \dfrac{[BrCl]^2}{[Br_2][Cl_2]} = 7.2$

The net sum of these two equations is

3. $2\,NOBr(g) + Cl_2(g) \rightleftharpoons 2\,NO(g) + 2\,BrCl(g)$

You can prove algebraically that the equilibrium-constant expression for reaction 3 is the product of the expressions for reactions 1 and 2:

$$K_c = \frac{[NO]^2[BrCl]^2}{[NOBr]^2[Cl_2]} = \frac{[NO]^2[Br_2]}{[NOBr]^2} \times \frac{[BrCl]^2}{[Br_2][Cl_2]}$$

Thus,

$$K_{c3} = (K_{c1})(K_{c2}) = (0.014)(7.2) = 0.10$$

To summarize:

1. The equilibrium constant of a reaction in the *reverse* direction is the *inverse* (or *reciprocal*) of the equilibrium constant of the reaction in the forward direction:

$$\begin{array}{ll} A + B \rightleftharpoons C + D & K_1 \\ C + D \rightleftharpoons A + B & K = 1/K_1 \end{array}$$

2. The equilibrium constant of a reaction that has been *multiplied* by a number is equal to the original equilibrium constant raised to a *power* equal to that number.

$$\begin{array}{ll} A + B \rightleftharpoons C + D & K_1 \\ nA + nB \rightleftharpoons nC + nD & K = K_1{}^n \end{array}$$

3. The equilibrium constant for a net reaction made up of *two or more reactions* is the *product* of the equilibrium constants for the individual reactions:

$$\begin{array}{ll} 1.\ A + B \rightleftharpoons C + D & K_1 \\ 2.\ C + F \rightleftharpoons G + A & K_2 \\ \hline 3.\ B + F \rightleftharpoons D + G & K_3 = (K_1)(K_2) \end{array}$$

SAMPLE EXERCISE 15.5 Combining Equilibrium Expressions

Given the reactions

$$\begin{array}{ll} HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) & K_c = 6.8 \times 10^{-4} \\ H_2C_2O_4(aq) \rightleftharpoons 2\,H^+(aq) + C_2O_4{}^{2-}(aq) & K_c = 3.8 \times 10^{-6} \end{array}$$

determine the value of K_c for the reaction

$$2\,HF(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons 2\,F^-(aq) + H_2C_2O_4(aq)$$

SOLUTION

Analyze We are given two equilibrium equations and the corresponding equilibrium constants and are asked to determine the equilibrium constant for a third equation, which is related to the first two.

Plan We cannot simply add the first two equations to get the third. Instead, we need to determine how to manipulate the equations to come up with the steps that will add to give us the desired equation.

Solve

If we multiply the first equation by 2 and make the corresponding change to its equilibrium constant (raising to the power 2), we get

$$2\,HF(aq) \rightleftharpoons 2\,H^+(aq) + 2\,F^-(aq) \qquad K_c = (6.8 \times 10^{-4})^2 = 4.6 \times 10^{-7}$$

Reversing the second equation and again making the corresponding change to its equilibrium constant (taking the reciprocal) gives

$$2\,H^+(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons H_2C_2O_4(aq) \qquad K_c = \frac{1}{3.8 \times 10^{-6}} = 2.6 \times 10^5$$

Now we have two equations that sum to give the net equation, and we can multiply the individual K_c values to get the desired equilibrium constant.

$$\begin{array}{rl} 2\,HF(aq) \rightleftharpoons 2\,H^+(aq) + 2\,F^-(aq) & K_c = 4.6 \times 10^{-7} \\ 2\,H^+(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons H_2C_2O_4(aq) & K_c = 2.5 \times 10^5 \\ \hline 2\,HF(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons 2\,F^-(aq) + H_2C_2O_4(aq) & K_c = (4.6 \times 10^{-7})(2.6 \times 10^5) = 0.12 \end{array}$$

PRACTICE EXERCISE

Given that, at 700 K, $K_p = 54.0$ for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$ and $K_p = 1.04 \times 10^{-4}$ for the reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, determine the value of K_p for the reaction $2\,NH_3(g) + 3\,I_2(g) \rightleftharpoons 6\,HI(g) + N_2(g)$ at 700 K.

Answer: $\dfrac{(54.0)^3}{1.04 \times 10^{-4}} = 1.51 \times 10^9$

15.4 | HETEROGENEOUS EQUILIBRIA

Many equilibria involve substances that are all in the same phase, usually gas or liquid. Such equilibria are called **homogeneous equilibria**. In some cases, however, the substances in equilibrium are in different phases, giving rise to **heterogeneous equilibria**. As an example of the latter, consider the equilibrium that occurs when solid lead(II) chloride dissolves in water to form a saturated solution:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,Cl^-(aq) \qquad [15.18]$$

This system consists of a solid in equilibrium with two aqueous species. If we want to write the equilibrium-constant expression for this process, we encounter a problem we have not encountered previously: How do we express the concentration of a solid? Although we can express that concentration in moles per unit volume, it is unnecessary to do so in writing equilibrium-constant expressions. *Whenever a pure solid or a pure liquid is involved in a heterogeneous equilibrium, its concentration is not included in the equilibrium-constant expression*. Thus, the equilibrium-constant expression for the reaction of Equation 15.18 is

$$K_c = [Pb^{2+}][Cl^-]^2 \qquad [15.19]$$

Even though $PbCl_2(s)$ does not appear in the equilibrium-constant expression, it must be present for equilibrium to occur.

The fact that pure solids and pure liquids are excluded from equilibrium-constant expressions can be explained in two ways. First, the concentration of a pure solid or liquid has a constant value. If the mass of a solid is doubled, its volume also doubles. Thus, its concentration, which relates to the ratio of mass to volume, stays the same. Because equilibrium-constant expressions include terms only for reactants and products whose concentrations can change during a chemical reaction, the concentrations of pure solids and pure liquids are omitted.

The omission can also be rationalized in a second way. Recall from Section 15.2 that what is substituted into a thermodynamic equilibrium expression is the activity of each substance, which is a ratio of the concentration to a reference value. For a pure substance, the reference value is the concentration of the pure substance, so that the activity of any pure solid or liquid is always 1.

GIVE IT SOME THOUGHT

Write the equilibrium-constant expression for the evaporation of water, $H_2O(l) \rightleftharpoons H_2O(g)$, in terms of partial pressures.

Decomposition of calcium carbonate is another example of a heterogeneous reaction:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Omitting the concentrations of the solids from the equilibrium-constant expression gives

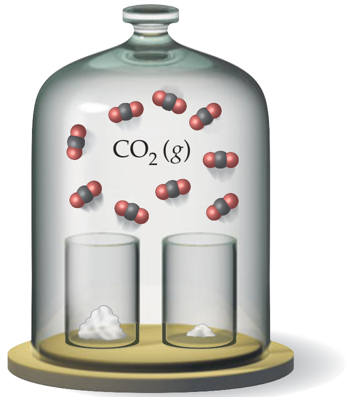
$$K_c = [CO_2] \quad \text{and} \quad K_p = P_{CO_2}$$

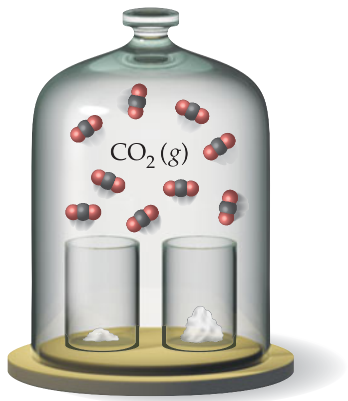
These equations tell us that at a given temperature, an equilibrium among $CaCO_3$, CaO, and CO_2 always leads to the same CO_2 partial pressure as long as all three components are present. As shown in ▶ **FIGURE 15.7**, we have the same CO_2 pressure regardless of the relative amounts of CaO and $CaCO_3$.

GO FIGURE

Imagine starting with only CaO in a bell jar and adding $CO_2(g)$ to make its pressure the same as it is in these two bell jars. How does the equilibrium concentration of $CO_2(g)$ in your jar compare with the $CO_2(g)$ equilibrium concentration in these two jars?

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$





▲ **FIGURE 15.7 At a given temperature, the equilibrium pressure of CO_2 in the bell jars is the same no matter how much of each solid is present.**

SAMPLE EXERCISE 15.6 Writing Equilibrium-Constant Expressions for Heterogeneous Reactions

Write the equilibrium-constant expression K_c for

(a) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$

(b) $SnO_2(s) + 2\,CO(g) \rightleftharpoons Sn(s) + 2\,CO_2(g)$

SOLUTION

Analyze We are given two chemical equations, both for heterogeneous equilibria, and asked to write the corresponding equilibrium-constant expressions.

Plan We use the law of mass action, remembering to omit any pure solids and pure liquids from the expressions.

Solve

(a) The equilibrium-constant expression is

$$K_c = \frac{[CO]}{[CO_2][H_2]}$$

Because H_2O appears in the reaction as a liquid, its concentration does not appear in the equilibrium-constant expression.

(b) The equilibrium-constant expression is

$$K_c = \frac{[CO_2]^2}{[CO]^2}$$

Because SnO_2 and Sn are pure solids, their concentrations do not appear in the equilibrium-constant expression.

PRACTICE EXERCISE

Write the following equilibrium-constant expressions:

(a) K_c for $Cr(s) + 3\,Ag^+(aq) \rightleftharpoons Cr^{3+}(aq) + 3\,Ag(s)$
(b) K_p for $3\,Fe(s) + 4\,H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4\,H_2(g)$

Answers: **(a)** $K_c = \dfrac{[Cr^{3+}]}{[Ag^+]^3}$ **(b)** $K_p = \dfrac{(P_{H_2})^4}{(P_{H_2O})^4}$

SAMPLE EXERCISE 15.7 Analyzing a Heterogeneous Equilibrium

Each of these mixtures was placed in a closed container and allowed to stand:

(a) $CaCO_3(s)$
(b) $CaO(s)$ and $CO_2(g)$ at a pressure greater than the value of K_p
(c) $CaCO_3(s)$ and $CO_2(g)$ at a pressure greater than the value of K_p
(d) $CaCO_3(s)$ and $CaO(s)$

Determine whether or not each mixture can attain the equilibrium

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

SOLUTION

Analyze We are asked which of several combinations of species can establish an equilibrium between calcium carbonate and its decomposition products, calcium oxide and carbon dioxide.

Plan For equilibrium to be achieved, it must be possible for both the forward process and the reverse process to occur. For the forward process to occur, there must be some calcium carbonate present. For the reverse process to occur, there must be both calcium oxide and carbon dioxide. In both cases, either the necessary compounds may be present initially or they may be formed by reaction of the other species.

Solve Equilibrium can be reached in all cases except (c) as long as sufficient quantities of solids are present. **(a)** $CaCO_3$ simply decomposes, forming $CaO(s)$ and $CO_2(g)$ until the equilibrium pressure of CO_2 is attained. There must be enough $CaCO_3$, however, to allow the CO_2 pressure to reach equilibrium. **(b)** CO_2 continues to combine with CaO until the partial pressure of the CO_2 decreases to the equilibrium value. **(c)** There is no CaO present, so equilibrium cannot be attained because there is no way the CO_2 pressure can decrease to its equilibrium value (which would require some of the CO_2 to react with CaO). **(d)** The situation is essentially the same as in (a): $CaCO_3$ decomposes until equilibrium is attained. The presence of CaO initially makes no difference.

PRACTICE EXERCISE

When added to $Fe_3O_4(s)$ in a closed container, which one of the following substances—$H_2(g)$, $H_2O(g)$, $O_2(g)$—allows equilibrium to be established in the reaction $3\,Fe(s) + 4\,H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4\,H_2(g)$?

Answer: $H_2(g)$

When a solvent is a reactant or product in an equilibrium, its concentration is omitted from the equilibrium-constant expression, provided the concentrations of reactants and products are low, so that the solvent is essentially a pure substance. Applying this guideline to an equilibrium involving water as a solvent,

$$H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons OH^-(aq) + HCO_3^-(aq) \qquad [15.20]$$

gives an equilibrium-constant expression that does not contain $[H_2O]$:

$$K_c = \frac{[OH^-][HCO_3^-]}{[CO_3^{2-}]} \qquad [15.21]$$

GIVE IT SOME THOUGHT

Write the equilibrium-constant expression for the reaction $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

15.5 CALCULATING EQUILIBRIUM CONSTANTS

If we can measure the equilibrium concentrations of all the reactants and products in a chemical reaction, as we did with the data in Table 15.1, calculating the value of the equilibrium constant is straightforward. We simply insert all the equilibrium concentrations into the equilibrium-constant expression for the reaction.

SAMPLE EXERCISE 15.8 Calculating *K* When All Equilibrium Concentrations Are Known

After a mixture of hydrogen and nitrogen gases in a reaction vessel is allowed to attain equilibrium at 472 °C, it is found to contain 7.38 atm H_2, 2.46 atm N_2, and 0.166 atm NH_3. From these data, calculate the equilibrium constant K_p for the reaction

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

SOLUTION

Analyze We are given a balanced equation and equilibrium partial pressures and are asked to calculate the value of the equilibrium constant.

Plan Using the balanced equation, we write the equilibrium-constant expression. We then substitute the equilibrium partial pressures into the expression and solve for K_p.

Solve

$$K_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{(0.166)^2}{(2.46)(7.38)^3} = 2.79 \times 10^{-5}$$

PRACTICE EXERCISE

An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25 °C: $[CH_3COOH] = 1.65 \times 10^{-2}\,M$; $[H^+] = 5.44 \times 10^{-4}\,M$; and $[CH_3COO^-] = 5.44 \times 10^{-4}\,M$. Calculate the equilibrium constant K_c for the ionization of acetic acid at 25 °C. The reaction is

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

Answer: 1.79×10^{-5}

Often we do not know the equilibrium concentrations of all species in an equilibrium mixture. If we know the equilibrium concentration of at least one species, however, we can generally use the stoichiometry of the reaction to deduce the equilibrium concentrations of the others. The following steps outline the procedure:

1. Tabulate all known initial and equilibrium concentrations of the species that appear in the equilibrium-constant expression.
2. For those species for which initial and equilibrium concentrations are known, calculate the change in concentration that occurs as the system reaches equilibrium.

3. Use the stoichiometry of the reaction (that is, the coefficients in the balanced chemical equation) to calculate the changes in concentration for all other species in the equilibrium-constant expression.
4. Use initial concentrations from step 1 and changes in concentration from step 3 to calculate any equilibrium concentrations not tabulated in step 1.
5. Determine the value of the equilibrium constant.

SAMPLE EXERCISE 15.9 Calculating *K* from Initial and Equilibrium Concentrations

A closed system initially containing $1.000 \times 10^{-3}\ M\ H_2$ and $2.000 \times 10^{-3}\ M\ I_2$ at 448 °C is allowed to reach equilibrium, and at equilibrium the HI concentration is $1.87 \times 10^{-3}\ M$. Calculate K_c at 448 °C for the reaction taking place, which is

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

SOLUTION

Analyze We are given the initial concentrations of H_2 and I_2 and the equilibrium concentration of HI. We are asked to calculate the equilibrium constant K_c for $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$.

Plan We construct a table to find equilibrium concentrations of all species and then use the equilibrium concentrations to calculate the equilibrium constant.

Solve First, we tabulate the initial and equilibrium concentrations of as many species as we can. We also provide space in our table for listing the changes in concentrations. As shown, it is convenient to use the chemical equation as the heading for the table.

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2\,HI(g)$
Initial concentration (*M*)	1.000×10^{-3}	2.000×10^{-3}	0
Change in concentration (*M*)			
Equilibrium concentration (*M*)			1.87×10^{-3}

Second, we calculate the change in HI concentration, which is the difference between the equilibrium and initial values:

$$\text{Change in [HI]} = 1.87 \times 10^{-3}\ M - 0 = 1.87 \times 10^{-3}\ M$$

Third, we use the coefficients in the balanced equation to relate the change in [HI] to the changes in $[H_2]$ and $[I_2]$:

$$\left(1.87 \times 10^{-3}\ \frac{\text{mol HI}}{\text{L}}\right)\left(\frac{1\ \text{mol}\ H_2}{2\ \text{mol HI}}\right) = 0.935 \times 10^{-3}\ \frac{\text{mol}\ H_2}{\text{L}}$$

$$\left(1.87 \times 10^{-3}\ \frac{\text{mol HI}}{\text{L}}\right)\left(\frac{1\ \text{mol}\ I_2}{2\ \text{mol HI}}\right) = 0.935 \times 10^{-3}\ \frac{\text{mol}\ I_2}{\text{L}}$$

Fourth, we calculate the equilibrium concentrations of H_2 and I_2, using initial concentrations and changes in concentration. The equilibrium concentration equals the initial concentration minus that consumed:

$$[H_2] = 1.000 \times 10^{-3}\ M - 0.935 \times 10^{-3}\ M = 0.065 \times 10^{-3}\ M$$

$$[I_2] = 2.000 \times 10^{-3}\ M - 0.935 \times 10^{-3}\ M = 1.065 \times 10^{-3}\ M$$

Our table now looks like this (with equilibrium concentrations in blue for emphasis):

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2\,HI(g)$
Initial concentration (*M*)	1.000×10^{-3}	2.000×10^{-3}	0
Change in concentration (*M*)	-0.935×10^{-3}	-0.935×10^{-3}	$+1.87 \times 10^{-3}$
Equilibrium concentration (*M*)	0.065×10^{-3}	1.065×10^{-3}	1.87×10^{-3}

Notice that the entries for the changes are negative when a reactant is consumed and positive when a product is formed.

Finally, we use the equilibrium-constant expression to calculate the equilibrium constant:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.87 \times 10^{-3})^2}{(0.065 \times 10^{-3})(1.065 \times 10^{-3})} = 51$$

Comment The same method can be applied to gaseous equilibrium problems to calculate K_p, in which case partial pressures are used as table entries in place of molar concentrations. Your instructor may refer to this kind of table as an ICE chart, where ICE stands for Initial – Change – Equilibrium.

PRACTICE EXERCISE

Sulfur trioxide decomposes at high temperature in a sealed container: $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$. Initially, the vessel is charged at 1000 K with $SO_3(g)$ at a partial pressure of 0.500 atm. At equilibrium the SO_3 partial pressure is 0.200 atm. Calculate the value of K_p at 1000 K.

Answer: 0.338

15.6 APPLICATIONS OF EQUILIBRIUM CONSTANTS

We have seen that the magnitude of K indicates the extent to which a reaction proceeds. If K is very large, the equilibrium mixture contains mostly substances on the product side of the equation for the reaction. (That is, the reaction proceeds far to the right.) If K is very small (that is, much less than 1), the equilibrium mixture contains mainly substances on the reactant side of the equation. The equilibrium constant also allows us to (1) predict the direction in which a reaction mixture achieves equilibrium and (2) calculate equilibrium concentrations of reactants and products.

Predicting the Direction of Reaction

For the formation of NH_3 from N_2 and H_2 (Equation 15.6), $K_c = 0.105$ at 472 °C. Suppose we place 2.00 mol of H_2, 1.00 mol of N_2, and 2.00 mol of NH_3 in a 1.00-L container at 472 °C. How will the mixture react to reach equilibrium? Will N_2 and H_2 react to form more NH_3, or will NH_3 decompose to N_2 and H_2?

To answer this question, we substitute the starting concentrations of N_2, H_2, and NH_3 into the equilibrium-constant expression and compare its value to the equilibrium constant:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(2.00)^2}{(1.00)(2.00)^3} = 0.500 \quad \text{whereas} \quad K_c = 0.105 \qquad [15.22]$$

To reach equilibrium, the quotient $[NH_3]^2/[N_2][H_2]^3$ must decrease from the starting value of 0.500 to the equilibrium value of 0.105. Because the system is closed, this change can happen only if $[NH_3]$ decreases and $[N_2]$ and $[H_2]$ increase. Thus, the reaction proceeds toward equilibrium by forming N_2 and H_2 from NH_3; that is, the reaction as written in Equation 15.6 proceeds from right to left.

This approach can be formalized by defining a quantity called the reaction quotient. The **reaction quotient**, Q, *is a number obtained by substituting reactant and product concentrations or partial pressures at any point during a reaction into an equilibrium-constant expression.* Therefore, for the general reaction

$$a\,A + b\,B \rightleftharpoons d\,D + e\,E$$

the reaction quotient in terms of molar concentrations is

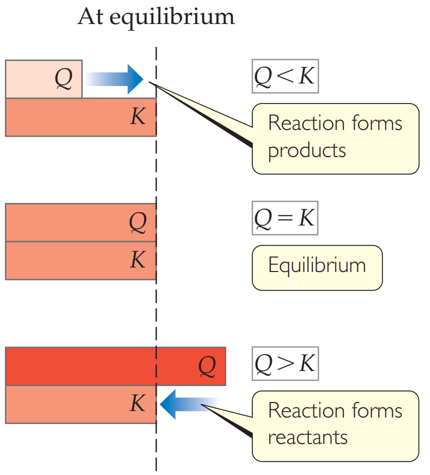
$$Q_c = \frac{[D]^d[E]^e}{[A]^a[B]^b} \qquad [15.23]$$

(A related quantity Q_p can be written for any reaction that involves gases by using partial pressures instead of concentrations.)

Although we use what looks like the equilibrium-constant expression to calculate the reaction quotient, the concentrations we use may or may not be the equilibrium concentrations. For example, when we substituted the starting concentrations into the equilibrium-constant expression of Equation 15.22, we obtained $Q_c = 0.500$ whereas $K_c = 0.105$. The equilibrium constant has only one value at each temperature. The reaction quotient, however, varies as the reaction proceeds.

Of what use is Q? One practical thing we can do with Q is tell whether our reaction really is at equilibrium, which is an especially valuable option when a reaction is very slow. We can take samples of our reaction mixture as the reaction proceeds, separate the components, and measure their concentrations. Then we insert these numbers into Equation 15.23 for our reaction. To determine whether or not we are at equilibrium, or in which direction the reaction proceeds to achieve equilibrium, we compare the values of Q_c and K_c or Q_p and K_p. Three possible situations arise:

- $Q = K$: The reaction quotient equals the equilibrium constant only if the system is at equilibrium.



▲ **FIGURE 15.8 Predicting the direction of a reaction by comparing *Q* and *K* at a given temperature.**

- $Q > K$: The concentration of products is too large and that of reactants too small. Substances on the right side of the chemical equation react to form substances on the left; the reaction proceeds from right to left to approach equilibrium.
- $Q < K$: The concentration of products is too small and that of reactants too large. The reaction achieves equilibrium by forming more products; it proceeds from left to right.

These relationships are summarized in ◄ **FIGURE 15.8**.

SAMPLE EXERCISE 15.10 Predicting the Direction of Approach to Equilibrium

At 448 °C the equilibrium constant K_c for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

is 50.5. Predict in which direction the reaction proceeds to reach equilibrium if we start with 2.0×10^{-2} mol of HI, 1.0×10^{-2} mol of H_2, and 3.0×10^{-2} mol of I_2 in a 2.00-L container.

SOLUTION

Analyze We are given a volume and initial molar amounts of the species in a reaction and asked to determine in which direction the reaction must proceed to achieve equilibrium.

Plan We can determine the starting concentration of each species in the reaction mixture. We can then substitute the starting concentrations into the equilibrium-constant expression to calculate the reaction quotient, Q_c. Comparing the magnitudes of the equilibrium constant, which is given, and the reaction quotient will tell us in which direction the reaction will proceed.

Solve

The initial concentrations are

$$[HI] = 2.0 \times 10^{-2}\ \text{mol}/2.00\ \text{L} = 1.0 \times 10^{-2}\ M$$
$$[H_2] = 1.0 \times 10^{-2}\ \text{mol}/2.00\ \text{L} = 5.0 \times 10^{-3}\ M$$
$$[I_2] = 3.0 \times 10^{-2}\ \text{mol}/2.00\ \text{L} = 1.5 \times 10^{-2}\ M$$

The reaction quotient is therefore

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.0 \times 10^{-2})^2}{(5.0 \times 10^{-3})(1.5 \times 10^{-2})} = 1.3$$

Because $Q_c < K_c$, the concentration of HI must increase and the concentrations of H_2 and I_2 must decrease to reach equilibrium; the reaction as written proceeds left to right to attain equilibrium.

PRACTICE EXERCISE

At 1000 K the value of K_p for the reaction $2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$ is 0.338. Calculate the value for Q_p, and predict the direction in which the reaction proceeds toward equilibrium if the initial partial pressures are $P_{SO_3} = 0.16$ atm; $P_{SO_2} = 0.41$ atm; $P_{O_2} = 2.5$ atm.

Answer: $Q_p = 16$; $Q_p > K_p$, and so the reaction will proceed from right to left, forming more SO_3.

Calculating Equilibrium Concentrations

Chemists frequently need to calculate the amounts of reactants and products present at equilibrium in a reaction for which they know the equilibrium constant. The approach in solving problems of this type is similar to the one we used for evaluating equilibrium constants: We tabulate initial concentrations or partial pressures, changes in those concentrations or pressures, and final equilibrium concentrations or partial pressures. Usually we end up using the equilibrium-constant expression to derive an equation that must be solved for an unknown quantity, as demonstrated in Sample Exercise 15.11.

SAMPLE EXERCISE 15.11 Calculating Equilibrium Concentrations

For the Haber process, $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, $K_p = 1.45 \times 10^{-5}$ at 500 °C. In an equilibrium mixture of the three gases at 500 °C, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 in this equilibrium mixture?

SOLUTION

Analyze We are given an equilibrium constant, K_p, and the equilibrium partial pressures of two of the three substances in the equation (N_2 and H_2), and we are asked to calculate the equilibrium partial pressure for the third substance (NH_3).

Plan We can set K_p equal to the equilibrium-constant expression and substitute in the partial pressures that we know. Then we can solve for the only unknown in the equation.

Solve We tabulate the equilibrium pressures:

	$N_2(g)$	$+\ 3\,H_2(g)$	$\rightleftharpoons 2\,NH_3(g)$
Equilibrium pressure (atm)	0.432	0.928	x

Because we do not know the equilibrium pressure of NH_3, we represent it with x. At equilibrium the pressures must satisfy the equilibrium-constant expression:

$$K_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{x^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

We now rearrange the equation to solve for x:

$$x^2 = (1.45 \times 10^{-5})(0.432)(0.928)^3 = 5.01 \times 10^{-6}$$

$$x = \sqrt{5.01 \times 10^{-6}} = 2.24 \times 10^{-3}\ \text{atm} = P_{NH_3}$$

Check We can always check our answer by using it to recalculate the value of the equilibrium constant:

$$K_p = \frac{(2.24 \times 10^{-3})^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

PRACTICE EXERCISE

At 500 K the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ has $K_p = 0.497$. In an equilibrium mixture at 500 K, the partial pressure of PCl_5 is 0.860 atm and that of PCl_3 is 0.350 atm. What is the partial pressure of Cl_2 in the equilibrium mixture?

Answer: 1.22 atm

In many situations we know the value of the equilibrium constant and the initial amounts of all species. We must then solve for the equilibrium amounts. Solving this type of problem usually entails treating the change in concentration as a variable. The stoichiometry of the reaction gives us the relationship between the changes in the amounts of all the reactants and products, as illustrated in Sample Exercise 15.12. The calculations frequently involve the quadratic formula, as you will see in this exercise.

SAMPLE EXERCISE 15.12 Calculating Equilibrium Concentrations from Initial Concentrations

A 1.000-L flask is filled with 1.000 mol of $H_2(g)$ and 2.000 mol of $I_2(g)$ at 448 °C. The value of the equilibrium constant K_c for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

at 448 °C is 50.5. What are the equilibrium concentrations of H_2, I_2, and HI in moles per liter?

SOLUTION

Analyze We are given the volume of a container, an equilibrium constant, and starting amounts of reactants in the container and are asked to calculate the equilibrium concentrations of all species.

Plan In this case we are not given any of the equilibrium concentrations. We must develop some relationships that relate the initial concentrations to those at equilibrium. The procedure is similar in many regards to that outlined in Sample Exercise 15.9, where we calculated an equilibrium constant using initial concentrations.

Solve First, we note the initial concentrations of H_2 and I_2:

$$[H_2] = 1.000\,M \quad \text{and} \quad [I_2] = 2.000\,M$$

Second, we construct a table in which we tabulate the initial concentrations:

	$H_2(g)$	$+\ I_2(g)$	$\rightleftharpoons 2\,HI(g)$
Initial concentration (M)	1.000	2.000	0
Change in concentration (M)			
Equilibrium concentration (M)			

Third, we use the stoichiometry of the reaction to determine the changes in concentration that occur as the reaction proceeds to equilibrium. The H_2 and I_2 concentrations will decrease as equilibrium is established and that of HI will increase. Let's represent the change in concentration of H_2 by x. The balanced chemical equation tells us the relationship between the changes in the concentrations of the three gases. For each x mol of H_2 that reacts, x mol of I_2 are consumed and $2x$ mol of HI are produced:

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2\,HI(g)$
Initial concentration (M)	1.000	2.000	0
Change in concentration (M)	$-x$	$-x$	$+2x$
Equilibrium concentration (M)			

Fourth, we use initial concentrations and changes in concentrations, as dictated by stoichiometry, to express the equilibrium concentrations. With all our entries, our table now looks like this:

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2\,HI(g)$
Initial concentration (M)	1.000	2.000	0
Change in concentration (M)	$-x$	$-x$	$+2x$
Equilibrium concentration (M)	$1.000 - x$	$2.000 - x$	$2x$

Fifth, we substitute the equilibrium concentrations into the equilibrium-constant expression and solve for x:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

If you have an equation-solving calculator, you can solve this equation directly for x. If not, expand this expression to obtain a quadratic equation in x:

$$4x^2 = 50.5(x^2 - 3.000x + 2.000)$$

$$46.5x^2 - 151.5x + 101.0 = 0$$

Solving the quadratic equation (Appendix A.3) leads to two solutions for x:

$$x = \frac{-(-151.5) \pm \sqrt{(-151.5)^2 - 4(46.5)(101.0)}}{2(46.5)} = 2.323 \text{ or } 0.935$$

When we substitute $x = 2.323$ into the expressions for the equilibrium concentrations, we find *negative* concentrations of H_2 and I_2. Because a negative concentration is not chemically meaningful, we reject this solution. We then use $x = 0.935$ to find the equilibrium concentrations:

$$[H_2] = 1.000 - x = 0.065\ M$$

$$[I_2] = 2.000 - x = 1.065\ M$$

$$[HI] = 2x = 1.87\ M$$

Check We can check our solution by putting these numbers into the equilibrium-constant expression to assure that we correctly calculate the equilibrium constant:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.87)^2}{(0.065)(1.065)} = 51$$

Comment Whenever you use a quadratic equation to solve an equilibrium problem, one of the solutions to the equation will give you a value that leads to negative concentrations and thus is not chemically meaningful. Reject this solution to the quadratic equation.

PRACTICE EXERCISE

For the equilibrium $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the equilibrium constant K_p is 0.497 at 500 K. A gas cylinder at 500 K is charged with $PCl_5(g)$ at an initial pressure of 1.66 atm. What are the equilibrium pressures of PCl_5, PCl_3, and Cl_2 at this temperature?

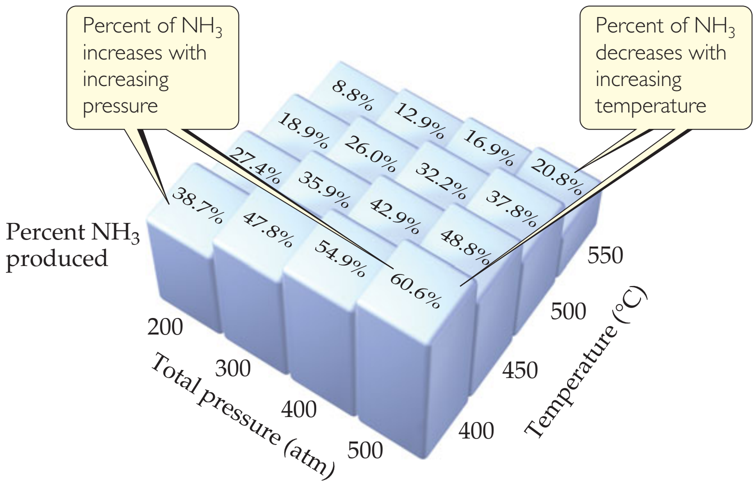
Answer: $P_{PCl_5} = 0.967$ atm, $P_{PCl_3} = P_{Cl_2} = 0.693$ atm

15.7 LE CHÂTELIER'S PRINCIPLE

Many of the products we use in everyday life are obtained from the chemical industry. Chemists and chemical engineers in industry spend a great deal of time and effort to maximize the yield of valuable products and minimize waste. For example, when Haber developed his process for making ammonia from N_2 and H_2, he examined how reaction conditions might be varied to increase yield. Using the values of the equilibrium constant at various temperatures, he calculated the equilibrium amounts of NH_3 formed under a variety of conditions. Some of Haber's results are shown in ▶ **FIGURE 15.9**.

GO FIGURE

At what combination of pressure and temperature should you run the reaction to maximize NH_3 yield?



▲ FIGURE 15.9 Effect of temperature and pressure on NH_3 yield in the Haber process. Each mixture was produced by starting with a 3:1 molar mixture of H_2 and N_2.

Notice that the percent of NH_3 present at equilibrium decreases with increasing temperature and increases with increasing pressure.

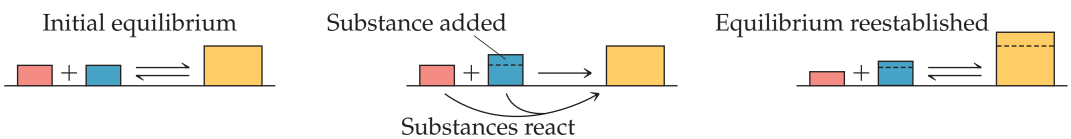
We can understand these effects in terms of a principle first put forward by Henri-Louis Le Châtelier* (1850–1936), a French industrial chemist: *If a system at equilibrium is disturbed by a change in temperature, pressure, or a component concentration, the system will shift its equilibrium position so as to counteract the effect of the disturbance.*

Le Chatelier's Principle

If a system at equilibrium is disturbed by a change in **concentration, pressure,** or **temperature,** the system will shift its equilibrium position so as to counter the effect of the disturbance.

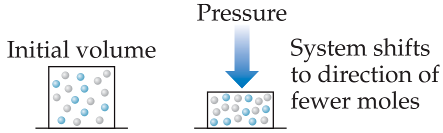
Concentration: adding or removing a reactant or product

If a substance is added to a system at equilibrium, the system reacts to consume some of the substance. If a substance is removed from a system, the system reacts to produce more of substance.



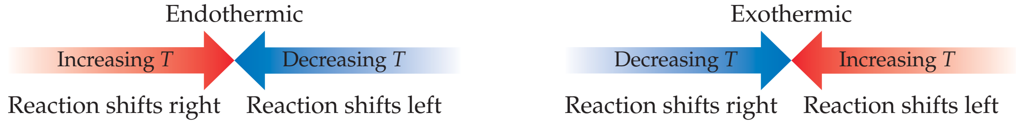
Pressure: changing the pressure by changing the volume

At constant temperature, reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas.



Temperature:

If the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the "excess reactant," namely heat.



*Pronounced "le-SHOT-lee-ay."

In this section we use Le Châtelier's principle to make qualitative predictions about how a system at equilibrium responds to various changes in external conditions. We consider three ways in which a chemical equilibrium can be disturbed: (1) adding or removing a reactant or product, (2) changing the pressure by changing the volume, and (3) changing the temperature.

Change in Reactant or Product Concentration

A system at dynamic equilibrium is in a state of balance. When the concentrations of species in the reaction are altered, the equilibrium shifts until a new state of balance is attained. What does *shift* mean? It means that reactant and product concentrations change over time to accommodate the new situation. *Shift* does *not* mean that the equilibrium constant itself is altered; the equilibrium constant remains the same. Le Châtelier's principle states that the shift is in the direction that minimizes or reduces the effect of the change. Therefore, *if a chemical system is already at equilibrium and the concentration of any substance in the mixture is increased (either reactant or product), the system reacts to consume some of that substance. Conversely, if the concentration of a substance is decreased, the system reacts to produce some of that substance.*

There is no change in the equilibrium constant when we change the concentrations of reactants or products. As an example, consider our familiar equilibrium mixture of N_2, H_2, and NH_3:

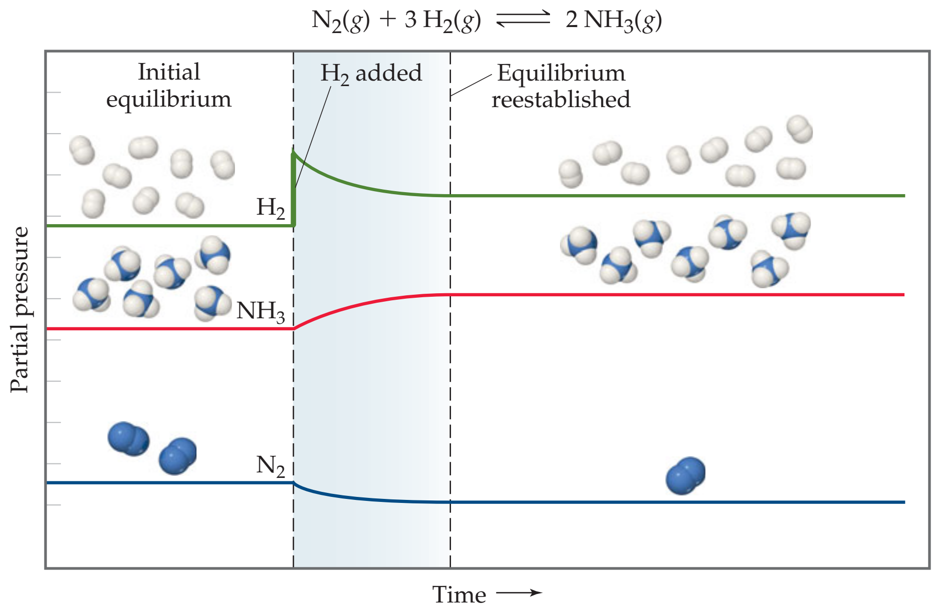
$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Adding H_2 causes the system to shift so as to reduce the increased concentration of H_2 (▼ **FIGURE 15.10**). This change can occur only if the reaction consumes H_2 and simultaneously consumes N_2 to form more NH_3. Adding N_2 to the equilibrium mixture likewise causes the reaction to shift toward forming more NH_3. Removing NH_3 also causes a shift toward producing more NH_3, whereas *adding* NH_3 to the system at equilibrium causes the reaction to shift in the direction that reduces the increased NH_3 concentration: Some of the added ammonia decomposes to form N_2 and H_2.

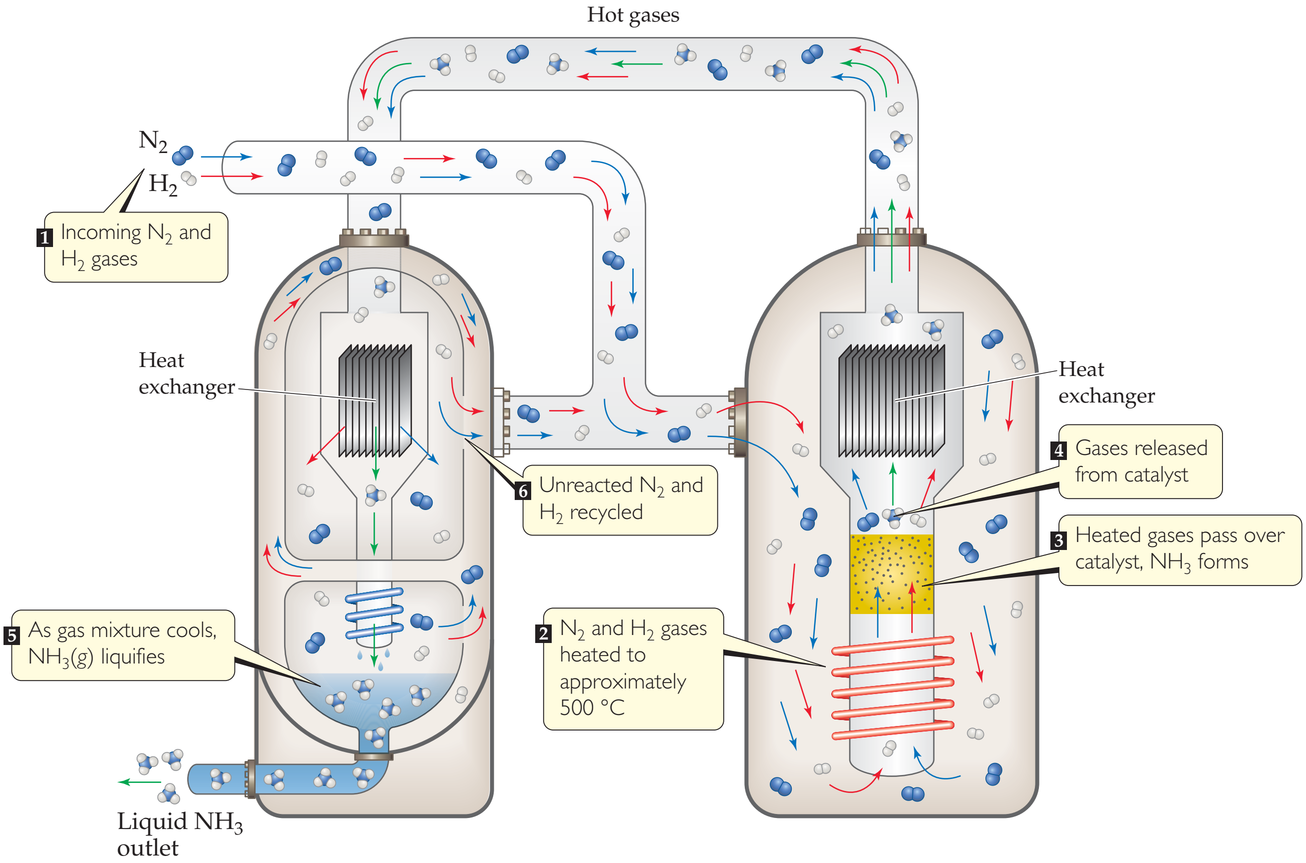
In the Haber reaction, therefore, removing NH_3 from an equilibrium mixture of N_2, H_2, and NH_3 causes the reaction to shift right to form more NH_3. If the NH_3 can be removed continuously as it is produced, the yield can be increased dramatically. In the

GO FIGURE

Why does the nitrogen concentration decrease after hydrogen is added?



▶ **FIGURE 15.10 Effect of adding H_2 to an equilibrium mixture of N_2, H_2, and NH_3.** Adding H_2 causes the reaction as written to shift to the right, consuming some H_2 to produce more NH_3.



▲ **FIGURE 15.11 Diagram of the industrial production of ammonia.** Incoming $N_2(g)$ and $H_2(g)$ are heated to approximately 500 °C and passed over a catalyst. When the resultant N_2, H_2, and NH_3 mixture is cooled, the NH_3 liquefies and is removed from the mixture, shifting the reaction to produce more NH_3.

industrial production of ammonia, the NH_3 is continuously removed by selectively liquefying it (▲ **FIGURE 15.11**). (The boiling point of NH_3, −33 °C, is much higher than those of N_2, −196 °C, and H_2, −253 °C.) The liquid NH_3 is removed, and the N_2 and H_2 are recycled to form more NH_3. As a result of the product being continuously removed, the reaction is driven essentially to completion.

GIVE IT SOME THOUGHT

What happens to the equilibrium $2\ NO(g) + O_2(g) \rightleftharpoons 2\ NO_2(g)$ if

a. O_2 is added to the system,

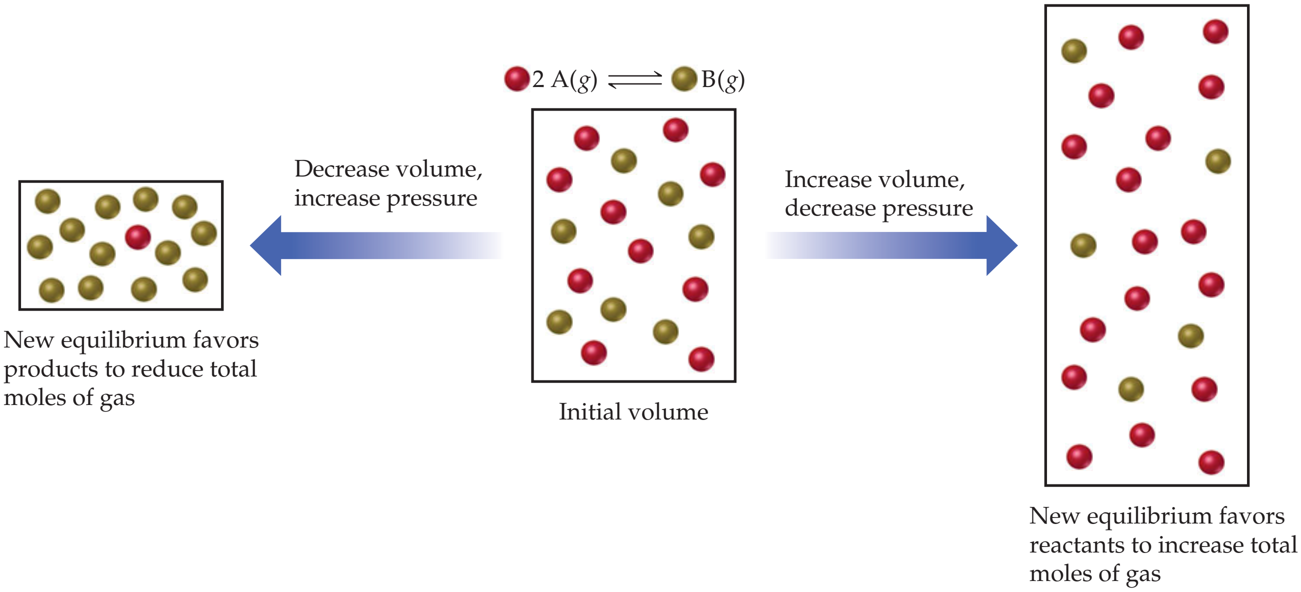
b. NO is removed?

Effects of Volume and Pressure Changes

If a system containing one or more gases is at equilibrium and its volume is decreased, thereby increasing its total pressure, Le Châtelier's principle indicates that the system responds by shifting its equilibrium position to reduce the pressure. A system can reduce its pressure by reducing the total number of gas molecules (fewer molecules of gas exert a lower pressure). Thus, at constant temperature, *reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas*. Increasing the volume causes a shift in the direction that produces more gas molecules (▶ **FIGURE 15.12**).

GIVE IT SOME THOUGHT

What happens to the equilibrium $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$ if the volume of the system is increased?



▲ **FIGURE 15.12** **Pressure and Le Châtelier's principle.**

In the reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, four molecules of reactant are consumed for every two molecules of product produced. Consequently, an increase in pressure (caused by a decrease in volume) shifts the reaction in the direction that produces fewer gas molecules, which leads to the formation of more NH_3, as indicated in Figure 15.9. In the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, the number of molecules of gaseous products (two) equals the number of molecules of gaseous reactants; therefore, changing the pressure does not influence the position of equilibrium.

Keep in mind that, as long as temperature remains constant, pressure-volume changes do *not* change the value of K. Rather, these changes alter the partial pressures of the gaseous substances. In Sample Exercise 15.8, we calculated $K_p = 2.79 \times 10^{-5}$ for the Haber reaction, $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, in an equilibrium mixture at 472 °C containing 7.38 atm H_2, 2.46 atm N_2, and 0.166 atm NH_3. Consider what happens when we suddenly reduce the volume of the system by one-half. If there were no shift in equilibrium, this volume change would cause the partial pressures of all substances to double, giving $P_{H_2} = 14.76$ atm, $P_{N_2} = 4.92$ atm, and $P_{NH_3} = 0.332$ atm. The reaction quotient would then no longer equal the equilibrium constant:

$$Q_p = \frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = \frac{(0.332)^2}{(4.92)(14.76)^3} = 6.97 \times 10^{-6} \neq K_p$$

Because $Q_p < K_p$, the system would no longer be at equilibrium. Equilibrium would be reestablished by increasing P_{NH_3} and/or decreasing P_{N_2} and P_{H_2} until $Q_p = K_p = 2.79 \times 10^{-5}$. Therefore, the equilibrium shifts to the right in the reaction as written, as Le Châtelier's principle predicts.

It is possible to change the pressure of a system in which a chemical reaction is running without changing its volume. For example, pressure increases if additional amounts of any reacting components are added to the system. We have already seen how to deal with a change in concentration of a reactant or product. The total pressure in the reaction vessel might also be increased by adding a gas that is not involved in the equilibrium. For example, argon might be added to the ammonia equilibrium system. The argon would not alter the partial pressures of any of the reacting components and therefore would not cause a shift in equilibrium.

Effect of Temperature Changes

Changes in concentrations or partial pressures shift equilibria without changing the value of the equilibrium constant. In contrast, almost every equilibrium constant changes as the temperature changes. For example, consider the equilibrium established when cobalt(II) chloride ($CoCl_2$) is dissolved in hydrochloric acid, HCl(*aq*), in the endothermic reaction

$$\underset{\text{Pale pink}}{Co(H_2O)_6^{\ 2+}(aq)} + 4\,Cl^-(aq) \rightleftharpoons \underset{\text{Deep blue}}{CoCl_4^{\ 2-}(aq)} + 6\,H_2O(l) \qquad \Delta H > 0 \qquad [15.24]$$

Because $Co(H_2O)_6^{\ 2+}$ is pink and $CoCl_4^{\ 2-}$ is blue, the position of this equilibrium is readily apparent from the color of the solution (▼ **FIGURE 15.13**). When the solution is heated it turns blue, indicating that the equilibrium has shifted to form more $CoCl_4^{\ 2-}$. Cooling the solution leads to a pink solution, indicating that the equilibrium has shifted to produce more $Co(H_2O)_6^{\ 2+}$. We can monitor this reaction by spectroscopic methods, measuring the concentration of all species at the different temperatures. (Section 14.2) We can then calculate the equilibrium constant at each temperature. How can we explain the fact that the equilibrium constants and therefore the position of equilibrium both depend on temperature?

We can deduce the rules for the relationship between K and temperature from Le Châtelier's principle. We do this by treating heat as a chemical reagent. In an *endothermic* (heat-absorbing) reaction, we consider heat a *reactant*, and in an *exothermic* (heat-releasing) reaction, we consider heat a *product*:

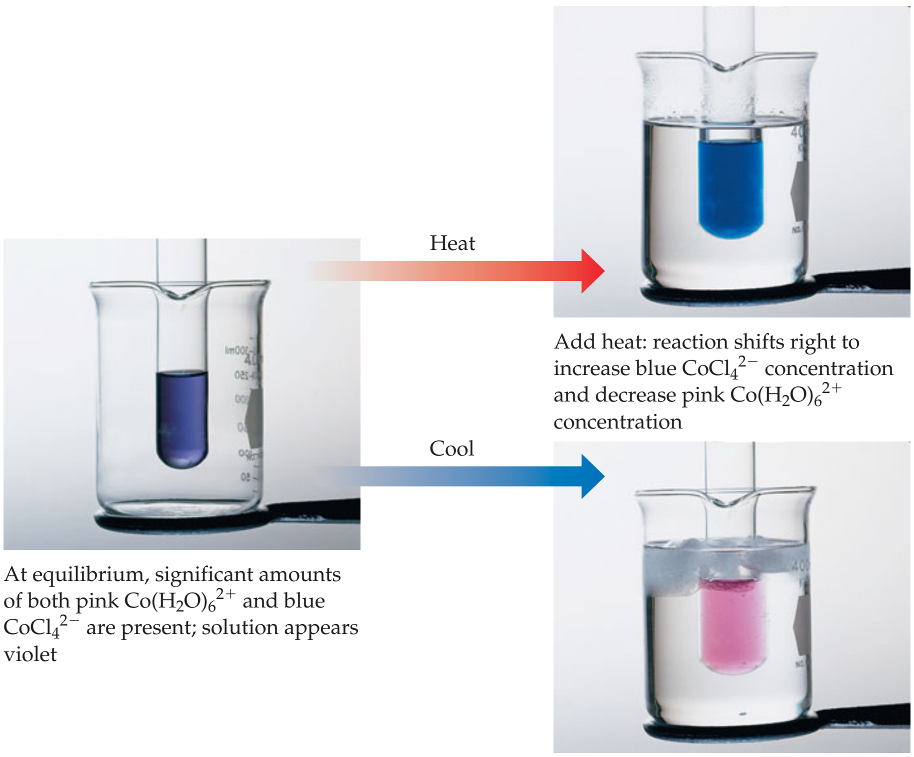
Endothermic: Reactants + *heat* $\rightleftharpoons$ products

Exothermic: Reactants $\rightleftharpoons$ products + *heat*

When the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the excess reactant (or product), namely heat.

$\Delta H > 0$, endothermic reaction

$$\text{Heat} + \underset{\text{Pink}}{Co(H_2O)_6^{\ 2+}(aq)} + 4\,Cl^-(aq) \rightleftharpoons \underset{\text{Blue}}{CoCl_4^{\ 2-}(aq)} + 6\,H_2O(l)$$



Add heat: reaction shifts right to increase blue $CoCl_4^{\ 2-}$ concentration and decrease pink $Co(H_2O)_6^{\ 2+}$ concentration

At equilibrium, significant amounts of both pink $Co(H_2O)_6^{\ 2+}$ and blue $CoCl_4^{\ 2-}$ are present; solution appears violet

Remove heat: reaction shifts left to decrease blue $CoCl_4^{\ 2-}$ concentration and increase pink $Co(H_2O)_6^{\ 2+}$ concentration

◀ **FIGURE 15.13 Temperature and Le Châtelier's principle.**

GIVE IT SOME THOUGHT

Use Le Châtelier's principle to explain why the equilibrium vapor pressure of a liquid increases with increasing temperature.

In an endothermic reaction, such as Equation 15.24, heat is absorbed as reactants are converted to products. Thus, increasing the temperature causes the equilibrium to shift to the right, in the direction of making more products, and K increases. In an exothermic reaction, the opposite occurs: Heat is produced as reactants are converted to products. Thus, increasing the temperature in this case causes the equilibrium to shift to the left, in the direction of making more reactants, and K decreases.

Endothermic: Increasing T results in higher K value

Exothermic: Increasing T results in lower K value

Cooling a reaction has the opposite effect. As we lower the temperature, the equilibrium shifts in the direction that produces heat. Thus, cooling an endothermic reaction shifts the equilibrium to the left, decreasing K, as shown in Figure 15.13, and cooling an exothermic reaction shifts the equilibrium to the right, increasing K.

SAMPLE EXERCISE 15.13 Using Le Châtelier's Principle to Predict Shifts in Equilibrium

Consider the equilibrium

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \qquad \Delta H^\circ = 58.0\ \text{kJ}$$

In which direction will the equilibrium shift when **(a)** N_2O_4 is added, **(b)** NO_2 is removed, **(c)** the pressure is increased by addition of $N_2(g)$, **(d)** the volume is increased, **(e)** the temperature is decreased?

SOLUTION

Analyze We are given a series of changes to be made to a system at equilibrium and are asked to predict what effect each change will have on the position of the equilibrium.

Plan Le Châtelier's principle can be used to determine the effects of each of these changes.

Solve

(a) The system will adjust to decrease the concentration of the added N_2O_4, so the equilibrium shifts to the right, in the direction of product.

(b) The system will adjust to the removal of NO_2 by shifting to the side that produces more NO_2; thus, the equilibrium shifts to the right.

(c) Adding N_2 will increase the total pressure of the system, but N_2 is not involved in the reaction. The partial pressures of NO_2 and N_2O_4 are therefore unchanged, and there is no shift in the position of the equilibrium.

(d) If the volume is increased, the system will shift in the direction that occupies a larger volume (more gas molecules); thus, the equilibrium shifts to the right.

(e) The reaction is endothermic, so we can imagine heat as a reagent on the reactant side of the equation. Decreasing the temperature will shift the equilibrium in the direction that produces heat, so the equilibrium shifts to the left, toward the formation of more N_2O_4. Note that only this last change also affects the value of the equilibrium constant, K.

PRACTICE EXERCISE

For the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H^\circ = 87.9\ \text{kJ}$$

in which direction will the equilibrium shift when **(a)** $Cl_2(g)$ is removed, **(b)** the temperature is decreased, **(c)** the volume of the reaction system is increased, **(d)** $PCl_3(g)$ is added?

Answers: **(a)** right, **(b)** left, **(c)** right, **(d)** left

SAMPLE EXERCISE 15.14 Predicting the Effect of Temperature on *K*

(a) Using the standard heat of formation data in Appendix C, determine the standard enthalpy change for the reaction

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

(b) Determine how the equilibrium constant for this reaction should change with temperature.

SOLUTION

Analyze We are asked to determine the standard enthalpy change of a reaction and how the equilibrium constant for the reaction varies with temperature.

Plan **(a)** We can use standard enthalpies of formation to calculate $\Delta H°$ for the reaction. **(b)** We can then use Le Châtelier's principle to determine what effect temperature will have on the equilibrium constant.

Solve

(a) Recall that the standard enthalpy change for a reaction is given by the sum of the standard molar enthalpies of formation of the products, each multiplied by its coefficient in the balanced chemical equation, less the same quantities for the reactants. (Section 5.7) At 25 °C, $\Delta H_f°$ for $NH_3(g)$ is −46.19 kJ/mol. The $\Delta H_f°$ values for $H_2(g)$ and $N_2(g)$ are zero by definition because the enthalpies of formation of the elements in their normal states at 25 °C are defined as zero. (Section 5.7) Because 2 mol of NH_3 is formed, the total enthalpy change is

$$(2\text{ mol})(-46.19\text{ kJ/mol}) - 0 = -92.38\text{ kJ}$$

(b) Because the reaction in the forward direction is exothermic, we can consider heat a product of the reaction. An increase in temperature causes the reaction to shift in the direction of less NH_3 and more N_2 and H_2. This effect is seen in the values for K_p presented in ▶ **TABLE 15.2**. Notice that K_p changes markedly with changes in temperature and that it is larger at lower temperatures.

Comment The fact that K_p for the formation of NH_3 from N_2 and H_2 decreases with increasing temperature is a matter of great practical importance. To form NH_3 at a reasonable rate requires higher temperatures. At higher temperatures, however, the equilibrium constant is smaller, and so the percentage conversion to NH_3 is smaller. To compensate for this, higher pressures are needed because high pressure favors NH_3 formation.

PRACTICE EXERCISE

Using the thermodynamic data in Appendix C, determine the enthalpy change for the reaction

$$2\,POCl_3(g) \rightleftharpoons 2\,PCl_3(g) + O_2(g)$$

Use this result to determine how the equilibrium constant for the reaction should change with temperature.

Answer: $\Delta H° = 508.3$ kJ; the equilibrium constant will increase with increasing temperature

TABLE 15.2 • Variation in K_p with Temperature for $N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$

Temperature (°C)	K_p
300	4.34×10^{-3}
400	1.64×10^{-4}
450	4.51×10^{-5}
500	1.45×10^{-5}
550	5.38×10^{-6}
600	2.25×10^{-6}

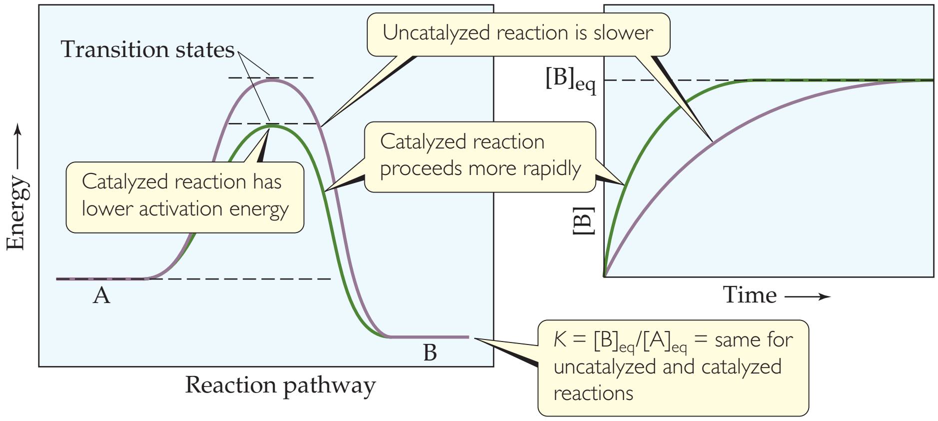
The Effect of Catalysts

What happens if we add a catalyst to a chemical system that is at equilibrium? As shown in ▶ **FIGURE 15.14**, (Figure 14.23) a catalyst lowers the activation barrier between reactants and products. The activation energies for both the forward and reverse reactions are lowered. The catalyst thereby increases the rates of both forward and reverse reactions. Since K is the ratio of the forward and reverse rate constants for a reaction, you can predict, correctly, that the presence of a catalyst, even though it changes the reaction *rate*, does not affect the numeric value of K (Figure 15.14). As a result, *a catalyst increases the rate at which equilibrium is achieved but does not change the composition of the equilibrium mixture.*

The rate at which a reaction approaches equilibrium is an important practical consideration. As an example, let's again consider the synthesis of ammonia from N_2 and H_2. In designing his process, Haber had to deal with a rapid decrease in the equilibrium constant with increasing temperature (Table 15.2). At temperatures sufficiently high to

GO FIGURE

How much faster is the catalyzed reaction compared to the uncatalyzed reaction?



▲ **FIGURE 15.14** **A catalyst increases the rate at which equilibrium is reached but does not change the overall composition of the mixture at equilibrium.**

give a satisfactory reaction rate, the amount of ammonia formed was too small. The solution to this dilemma was to develop a catalyst that would produce a reasonably rapid approach to equilibrium at a sufficiently low temperature, so that the equilibrium constant remained reasonably large. The development of a suitable catalyst thus became the focus of Haber's research efforts.

After trying different substances to see which would be most effective, Carl Bosch (see "Chemistry Put to Work: The Haber Process," page 615) settled on iron mixed with metal oxides, and variants of this catalyst formulation are still used today. These catalysts make it possible to obtain a reasonably rapid approach to equilibrium at around 400 to 500 °C and 200 to 600 atm. The high pressures are needed to obtain a satisfactory equilibrium amount of NH_3. If chemists and chemical engineers could identify a catalyst that leads to sufficiently rapid reaction at temperatures lower than 400 °C, it would be possible to obtain the same extent of equilibrium conversion at pressures much lower than 200 to 600 atm. This would result in great savings in the cost of the high-pressure equipment used in ammonia synthesis today.

As noted in Section 15.2, our need for nitrogen as fertilizer is growing globally, making the fixation of nitrogen a process of ever-increasing importance.

GIVE IT SOME THOUGHT

Does the addition of a catalyst have any effect on the position of an equilibrium?

SAMPLE INTEGRATIVE EXERCISE Putting Concepts Together

At temperatures near 800 °C, steam passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H_2:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

The mixture of gases that results is an important industrial fuel called *water gas*. **(a)** At 800 °C the equilibrium constant for this reaction is $K_p = 14.1$. What are the equilibrium partial pressures of H_2O, CO, and H_2 in the equilibrium mixture at this temperature if we start with solid carbon and 0.100 mol of H_2O in a 1.00-L vessel? **(b)** What is the minimum amount of carbon required to achieve equilibrium under these conditions? **(c)** What is the total pressure in the vessel at equilibrium? **(d)** At 25 °C the value of K_p for this reaction is 1.7×10^{-21}. Is the reaction exothermic or endothermic? **(e)** To produce the maximum amount of CO and H_2 at equilibrium, should the pressure of the system be increased or decreased?

SOLUTION

(a) To determine the equilibrium partial pressures, we use the ideal-gas equation, first determining the starting partial pressure of hydrogen.

$$P_{H_2O} = \frac{n_{H_2O}RT}{V} = \frac{(0.100 \text{ mol})(0.08206 \text{ L-atm/mol-K})(1073 \text{ K})}{1.00 \text{ L}} = 8.81 \text{ atm}$$

We then construct a table of initial partial pressures and their changes as equilibrium is achieved:

	$C(s)$ +	$H_2O(g)$ $\rightleftharpoons$	$CO(g)$ +	$H_2(g)$
Initial partial pressure (atm)		8.81	0	0
Change in partial pressure (atm)		$-x$	$+x$	$+x$
Equilibrium partial pressure (atm)		$8.81 - x$	x	x

There are no entries in the table under $C(s)$ because the reactant, being a solid, does not appear in the equilibrium-constant expression. Substituting the equilibrium partial pressures of the other species into the equilibrium-constant expression for the reaction gives

$$K_p = \frac{P_{CO}P_{H_2}}{P_{H_2O}} = \frac{(x)(x)}{(8.81 - x)} = 14.1$$

Multiplying through by the denominator gives a quadratic equation in x:

$$x^2 = (14.1)(8.81 - x)$$
$$x^2 + 14.1x - 124.22 = 0$$

Solving this equation for x using the quadratic formula yields $x = 6.14$ atm. Hence, the equilibrium partial pressures are $P_{CO} = x = 6.14$ atm, $P_{H_2} = x = 6.14$ atm, and $P_{H_2O} = (8.81 - x) = 2.67$ atm.

(b) Part (a) shows that $x = 6.14$ atm of H_2O must react for the system to achieve equilibrium. We can use the ideal-gas equation to convert this partial pressure into a mole amount.

$$n = \frac{PV}{RT} = \frac{(6.14 \text{ atm})(1.00 \text{ L})}{(0.08206 \text{ L-atm/mol-K})(1073 \text{ K})} = 0.0697 \text{ mol}$$

Thus, 0.0697 mol of H_2O and the same amount of C must react to achieve equilibrium. As a result, there must be at least 0.0697 mol of C (0.836 g C) present among the reactants at the start of the reaction.

(c) The total pressure in the vessel at equilibrium is simply the sum of the equilibrium partial pressures:

$$P_{total} = P_{H_2O} + P_{CO} + P_{H_2} = 2.67 \text{ atm} + 6.14 \text{ atm} + 6.14 \text{ atm} = 14.95 \text{ atm}$$

(d) In discussing Le Châtelier's principle, we saw that endothermic reactions exhibit an increase in K_p with increasing temperature. Because the equilibrium constant for this reaction increases as temperature increases, the reaction must be endothermic. From the enthalpies of formation given in Appendix C, we can verify our prediction by calculating the enthalpy change for the reaction, $\Delta H° = \Delta H_f°(CO(g)) + \Delta H_f°(H_2(g)) - \Delta H_f°(C(s, \text{graphite})) - \Delta H_f°(H_2O(g)) = +131.3$ KJ. The positive sign for $\Delta H°$ indicates that the reaction is endothermic.

(e) According to Le Châtelier's principle, a decrease in the pressure causes a gaseous equilibrium to shift toward the side of the equation with the greater number of moles of gas. In this case there are two moles of gas on the product side and only one on the reactant side. Therefore, the pressure should be decreased to maximize the yield of the CO and H_2.

CHEMISTRY PUT TO WORK

Controlling Nitric Oxide Emissions

The formation of NO from N_2 and O_2,

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g) \qquad \Delta H^\circ = 90.4 \text{ kJ} \qquad [15.25]$$

provides an interesting example of the practical importance of the fact that equilibrium constants and reaction rates change with temperature. By applying Le Châtelier's principle to this endothermic reaction and treating heat as a reactant, we deduce that an increase in temperature shifts the equilibrium in the direction of more NO. The equilibrium constant K_p for formation of 1 mol of NO from its elements at 300 K is only about 1×10^{-15} (▶ **FIGURE 15.15**). At 2400 K, however, the equilibrium constant is about 0.05, which is 10^{13} times larger than the 300 K value.

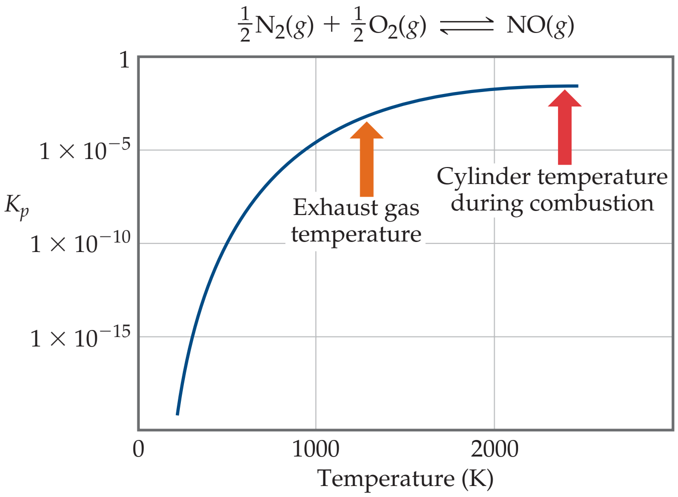
Figure 15.15 helps explain why NO is a pollution problem. In the cylinder of a modern high-compression automobile engine, the temperature during the fuel-burning part of the cycle is approximately 2400 K. Also, there is a fairly large excess of air in the cylinder. These conditions favor the formation of NO. After combustion, however, the gases cool quickly. As the temperature drops, the equilibrium in Equation 15.25 shifts to the left (because the reactant heat is being removed). The lower temperature also means that the reaction rate decreases, however, so the NO formed at 2400 K is essentially "frozen" in that form as the gas cools.

The gases exhausting from the cylinder are still quite hot, perhaps 1200 K. At this temperature, as shown in Figure 15.15, the equilibrium constant for formation of NO is about 5×10^{-4}, much smaller than the value at 2400 K. However, the rate of conversion of NO to N_2 and O_2 is too slow to permit much loss of NO before the gases are cooled further.

As discussed in the "Chemistry Put to Work" box in Section 14.7, one of the goals of automotive catalytic converters is to achieve rapid conversion of NO to N_2 and O_2 at the temperature of the exhaust gas. Some catalysts developed for this reaction are reasonably effective under the grueling conditions in automotive exhaust systems. Nevertheless, scientists and engineers are continuously searching for new materials that provide even more effective catalysis of the decomposition of nitrogen oxides.

GO FIGURE

Estimate the value of K_p at 1200 K, the exhaust gas temperature.



▲ **FIGURE 15.15 Equilibrium and temperature.** The equilibrium constant increases with increasing temperature because the reaction is endothermic. It is necessary to use a log scale for K_p because the values vary over such a large range.

CHAPTER SUMMARY AND KEY TERMS

INTRODUCTION AND SECTION 15.1 A chemical reaction can achieve a state in which the forward and reverse processes are occurring at the same rate. This condition is called **chemical equilibrium**, and it results in the formation of an equilibrium mixture of the reactants and products of the reaction. The composition of an equilibrium mixture does not change with time if temperature is held constant.

SECTION 15.2 An equilibrium that is used throughout this chapter is the reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$. This reaction is the basis of the **Haber process** for the production of ammonia. The relationship between the concentrations of the reactants and products of a system at equilibrium is given by the **law of mass action**. For an equilibrium equation of the form $a\,A + b\,B \rightleftharpoons d\,D + e\,E$, the **equilibrium-constant expression** is written as

$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$$

where K_c is a constant called the **equilibrium constant**. When the equilibrium system of interest consists of gases, it is often convenient to express the concentrations of reactants and products in terms of gas pressures:

$$K_p = \frac{(P_D)^d(P_E)^e}{(P_A)^a(P_B)^b}$$

K_c and K_p are related by the expression $K_p = K_c(RT)^{\Delta n}$.

SECTION 15.3 The value of the equilibrium constant changes with temperature. A large value of K_c indicates that the equilibrium mixture contains more products than reactants and therefore lies toward the product side of the equation. A small value for the equilibrium constant means that the equilibrium mixture contains less products than reactants and therefore lies toward the reactant side. The equilibrium-constant expression and the equilibrium constant of the reverse of a reaction are the reciprocals of those of the forward reaction. If a reaction is the sum of two or more reactions, its equilibrium constant will be the product of the equilibrium constants for the individual reactions.

SECTION 15.4 Equilibria for which all substances are in the same phase are called **homogeneous equilibria**; in **heterogeneous equilibria** two or more phases are present. The concentrations of pure solids and liquids are left out of the equilibrium-constant expression for a heterogeneous equilibrium.

SECTION 15.5 If the concentrations of all species in an equilibrium are known, the equilibrium-constant expression can be used to calculate the equilibrium constant. The changes in the concentrations of reactants and products on the way to achieving equilibrium are governed by the stoichiometry of the reaction.

SECTION 15.6 The **reaction quotient**, Q, is found by substituting reactant and product concentrations or partial pressures at any point during a reaction into the equilibrium-constant expression. If the system is at equilibrium, $Q = K$. If $Q \neq K$, however, the system is not at equilibrium. When $Q < K$, the reaction will move toward equilibrium by forming more products (the reaction proceeds from left to right); when $Q > K$, the reaction will proceed from right to left. Knowing the value of K makes it possible to calculate the equilibrium amounts of reactants and products, often by the solution of an equation in which the unknown is the change in a partial pressure or concentration.

SECTION 15.7 **Le Châtelier's principle** states that if a system at equilibrium is disturbed, the equilibrium will shift to minimize the disturbing influence. By this principle, if a reactant or product is added to a system at equilibrium, the equilibrium will shift to consume the added substance. The effects of removing reactants or products and of changing the pressure or volume of a reaction can be similarly deduced. For example, if the volume of the system is reduced, the equilibrium will shift in the direction that decreases the number of gas molecules. The enthalpy change for a reaction indicates how an increase in temperature affects the equilibrium: For an endothermic reaction, an increase in temperature shifts the equilibrium to the right; for an exothermic reaction, a temperature increase shifts the equilibrium to the left. Catalysts affect the speed at which equilibrium is reached but do not affect the magnitude of K.

KEY SKILLS

- Understand what is meant by chemical equilibrium and how it relates to reaction rates (Section 15.1).
- Write the equilibrium-constant expression for any reaction (Section 15.2).
- Relate K_c and K_p (Section 15.2).
- Relate the magnitude of an equilibrium constant to the relative amounts of reactants and products present in an equilibrium mixture (Section 15.3).
- Manipulate the equilibrium constant to reflect changes in the chemical equation (Section 15.3).
- Write the equilibrium-constant expression for a heterogeneous reaction (Section 15.4).
- Calculate an equilibrium constant from concentration measurements (Section 15.5).
- Predict the direction of a reaction given the equilibrium constant and the concentrations of reactants and products (Section 15.6).
- Calculate equilibrium concentrations given the equilibrium constant and all but one equilibrium concentration (Section 15.6).
- Calculate equilibrium concentrations, given the equilibrium constant and the starting concentrations (Section 15.6).
- Understand how changing the concentrations, volume, or temperature of a system at equilibrium affects the equilibrium position (Section 15.7).

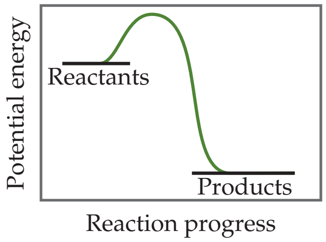
KEY EQUATIONS

- $K_c = \dfrac{[\mathrm{D}]^d[\mathrm{E}]^e}{[\mathrm{A}]^a[\mathrm{B}]^b}$ [15.8] The equilibrium-constant expression for a general reaction of the type $a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons d\,\mathrm{D} + e\,\mathrm{E}$; the concentrations are equilibrium concentrations only
- $K_p = \dfrac{(P_\mathrm{D})^d(P_\mathrm{E})^e}{(P_\mathrm{A})^a(P_\mathrm{B})^b}$ [15.11] The equilibrium-constant expression in terms of equilibrium partial pressures
- $K_p = K_c(RT)^{\Delta n}$ [15.14] Relating the equilibrium constant based on pressures to the equilibrium constant based on concentration
- $Q_c = \dfrac{[\mathrm{D}]^d[\mathrm{E}]^e}{[\mathrm{A}]^a[\mathrm{B}]^b}$ [15.23] The reaction quotient. The concentrations are for any time during a reaction. If the concentrations are equilibrium concentrations, then $Q_c = K_c$.

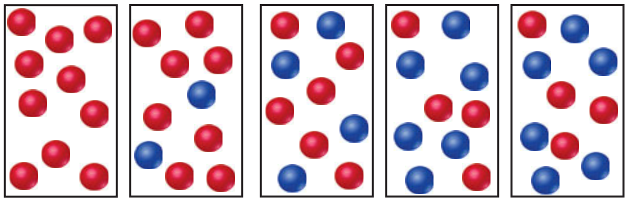
EXERCISES

VISUALIZING CONCEPTS

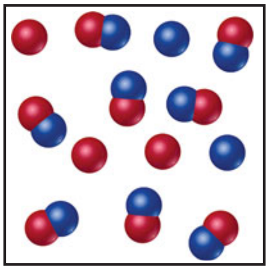
15.1 (**a**) Based on the following energy profile, predict whether $k_f > k_r$ or $k_f < k_r$. (**b**) Using Equation 15.5, predict whether the equilibrium constant for the process is greater than 1 or less than 1. [Section 15.1]



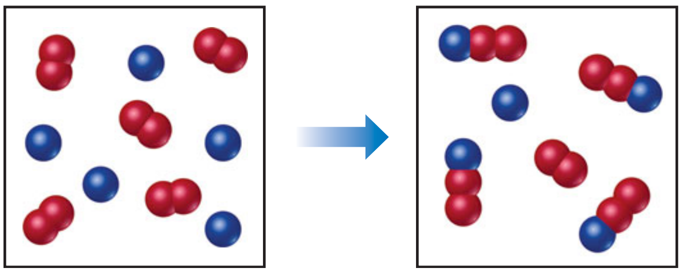
15.2 The following diagrams represent a hypothetical reaction $A \longrightarrow B$, with A represented by red spheres and B represented by blue spheres. The sequence from left to right represents the system as time passes. Do the diagrams indicate that the system reaches an equilibrium state? Explain. [Sections 15.1 and 15.2]



15.3 The following diagram represents an equilibrium mixture produced for a reaction of the type $A + X \rightleftharpoons AX$. If the volume is 1 L, is K greater or smaller than 1? [Section 15.2]



15.4 The following diagram represents a reaction shown going to completion. (**a**) Letting A = red spheres and B = blue spheres, write a balanced equation for the reaction. (**b**) Write the equilibrium-constant expression for the reaction. (**c**) Assuming that all of the molecules are in the gas phase, calculate Δn, the change in the number of gas molecules that accompanies the reaction. (**d**) How can you calculate K_p if you know K_c at a particular temperature? [Section 15.2]



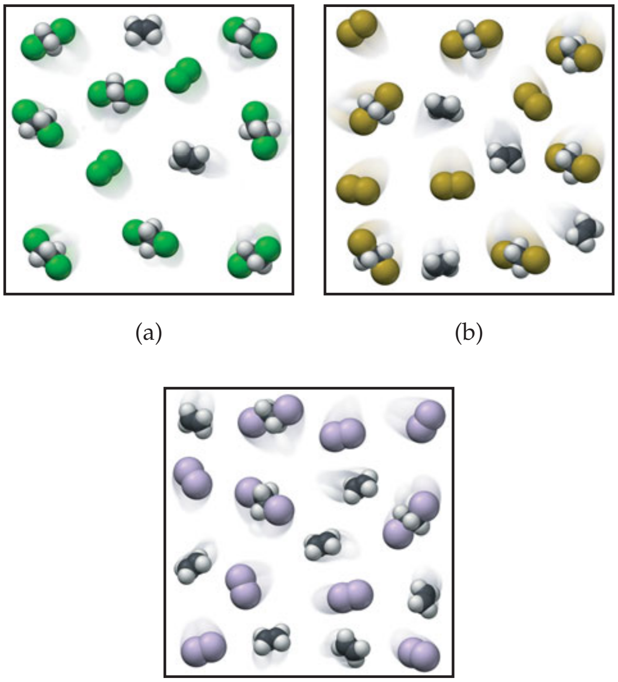
15.5 A friend says that the faster the reaction, the larger the equilibrium constant. Is your friend correct? Why or why not? [Sections 15.1 and 15.2]

15.6 A certain chemical reaction has $K_c = 1.5 \times 10^6$. Does this mean that at equilibrium there are 1.5×10^6 times as many product molecules as reactant molecules? Explain. [Sections 15.1 and 15.2]

15.7 Ethene (C_2H_4) reacts with halogens (X_2) by the following reaction:

$$C_2H_4(g) + X_2(g) \rightleftharpoons C_2H_4X_2(g)$$

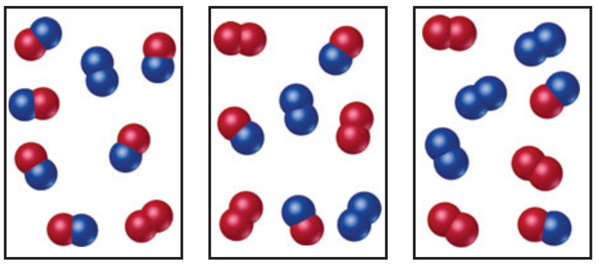
The following figures represent the concentrations at equilibrium at the same temperature when X_2 is Cl_2 (green), Br_2 (brown), and I_2 (purple). List the equilibria from smallest to largest equilibrium constant. [Section 15.3]



(a) (b)

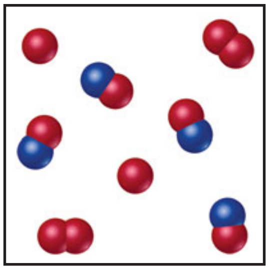
(c)

15.8 The reaction $A_2 + B_2 \rightleftharpoons 2\,AB$ has an equilibrium constant $K_c = 1.5$. The following diagrams represent reaction mixtures containing A_2 molecules (red), B_2 molecules (blue), and AB molecules. (**a**) Which reaction mixture is at equilibrium? (**b**) For those mixtures that are not at equilibrium, how will the reaction proceed to reach equilibrium? [Sections 15.5 and 15.6]

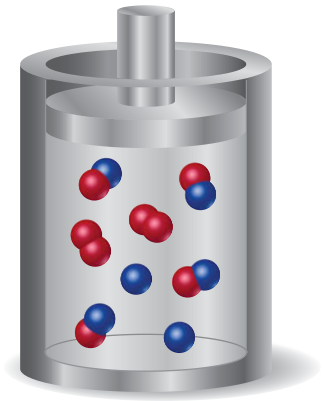


(i) (ii) (iii)

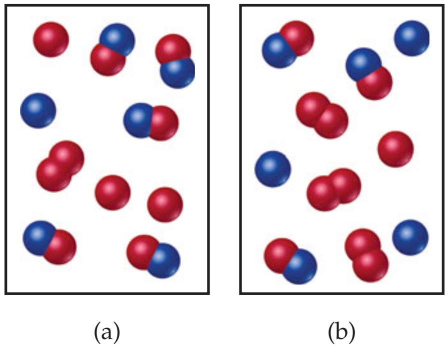
15.9 The reaction $A_2(g) + B(g) \rightleftharpoons A(g) + AB(g)$ has an equilibrium constant of $K_p = 2$. The accompanying diagram shows a mixture containing A atoms (red), A_2 molecules, and AB molecules (red and blue). How many B atoms should be added to the diagram to illustrate an equilibrium mixture? [Section 15.6]



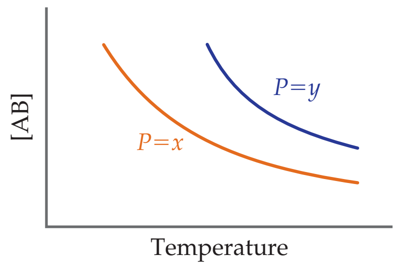
15.10 The diagram shown here represents the equilibrium state for the reaction $A_2(g) + 2\,B(g) \rightleftharpoons 2\,AB(g)$. **(a)** Assuming the volume is 2 L, calculate the equilibrium constant K_c for the reaction. **(b)** If the volume of the equilibrium mixture is decreased, will the number of AB molecules increase or decrease? [Sections 15.5 and 15.7]



15.11 The following diagrams represent equilibrium mixtures for the reaction $A_2 + B \rightleftharpoons A + AB$ at (a) 300 K and (b) 500 K. The A atoms are red, and the B atoms are blue. Is the reaction exothermic or endothermic? [Section 15.7]



15.12 The following graph represents the yield of the compound AB at equilibrium in the reaction $A(g) + B(g) \longrightarrow AB(g)$ at two different pressures, x and y, as a function of temperature.



(a) Is this reaction exothermic or endothermic? **(b)** Is $P = x$ greater or smaller than $P = y$? [Section 15.7]

EQUILIBRIUM; THE EQUILIBRIUM CONSTANT (sections 15.1, 15.2, 15.3, 15.4)

15.13 Suppose that the gas-phase reactions $A \longrightarrow B$ and $B \longrightarrow A$ are both elementary processes with rate constants of $4.7 \times 10^{-3}\ s^{-1}$ and $5.8 \times 10^{-1}\ s^{-1}$, respectively. **(a)** What is the value of the equilibrium constant for the equilibrium $A(g) \rightleftharpoons B(g)$? **(b)** Which is greater at equilibrium, the partial pressure of A or the partial pressure of B? Explain.

15.14 Consider the reaction $A + B \rightleftharpoons C + D$. Assume that both the forward reaction and the reverse reaction are elementary processes and that the value of the equilibrium constant is very large. **(a)** Which species predominate at equilibrium, reactants or products? **(b)** Which reaction has the larger rate constant, the forward or the reverse? Explain.

15.15 Write the expression for K_c for the following reactions. In each case indicate whether the reaction is homogeneous or heterogeneous.

(a) $3\,NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$
(b) $CH_4(g) + 2\,H_2S(g) \rightleftharpoons CS_2(g) + 4\,H_2(g)$
(c) $Ni(CO)_4(g) \rightleftharpoons Ni(s) + 4\,CO(g)$
(d) $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$
(e) $2\,Ag(s) + Zn^{2+}(aq) \rightleftharpoons 2\,Ag^+(aq) + Zn(s)$
(f) $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$
(g) $2\,H_2O(l) \rightleftharpoons 2\,H^+(aq) + 2\,OH^-(aq)$

15.16 Write the expressions for K_c for the following reactions. In each case indicate whether the reaction is homogeneous or heterogeneous.

(a) $2\,O_3(g) \rightleftharpoons 3\,O_2(g)$
(b) $Ti(s) + 2\,Cl_2(g) \rightleftharpoons TiCl_4(l)$
(c) $2\,C_2H_4(g) + 2\,H_2O(g) \rightleftharpoons 2\,C_2H_6(g) + O_2(g)$
(d) $C(s) + 2\,H_2(g) \rightleftharpoons CH_4(g)$
(e) $4\,HCl(aq) + O_2(g) \rightleftharpoons 2\,H_2O(l) + 2\,Cl_2(g)$
(f) $2\,C_8H_{18}(l) + 25\,O_2(g) \rightleftharpoons 16\,CO_2(g) + 18\,H_2O(g)$
(g) $2\,C_8H_{18}(l) + 25\,O_2(g) \rightleftharpoons 16\,CO_2(g) + 18\,H_2O(l)$

15.17 When the following reactions come to equilibrium, does the equilibrium mixture contain mostly reactants or mostly products?

(a) $N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g);\ K_c = 1.5 \times 10^{-10}$
(b) $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g);\ K_p = 2.5 \times 10^9$

15.18 Which of the following reactions lies to the right, favoring the formation of products, and which lies to the left, favoring formation of reactants?
(a) $2\ NO(g) + O_2(g) \rightleftharpoons 2\ NO_2(g)$; $K_p = 5.0 \times 10^{12}$
(b) $2\ HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$; $K_c = 5.8 \times 10^{-18}$

15.19 Can the equilibrium constant ever be a negative number? Explain.

15.20 Can the equilibrium constant ever be zero? Explain.

15.21 If $K_c = 0.042$ for $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ at 500 K, what is the value of K_p for this reaction at this temperature?

15.22 Calculate K_c at 303 K for $SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g)$ if $K_p = 34.5$ at this temperature.

15.23 The equilibrium constant for the reaction

$$2\ NO(g) + Br_2(g) \rightleftharpoons 2\ NOBr(g)$$

is $K_c = 1.3 \times 10^{-2}$ at 1000 K. **(a)** At this temperature does the equilibrium favor NO and Br_2, or does it favor NOBr? **(b)** Calculate K_c for $2\ NOBr(g) \rightleftharpoons 2\ NO(g) + Br_2(g)$. **(c)** Calculate K_c for $NOBr(g) \longrightarrow NO(g) + \frac{1}{2} Br_2(g)$.

15.24 Consider the following equilibrium:

$$2\ H_2(g) + S_2(g) \rightleftharpoons 2\ H_2S(g) \quad K_c = 1.08 \times 10^7 \text{ at } 700\ °C$$

(a) Calculate K_p. **(b)** Does the equilibrium mixture contain mostly H_2 and S_2 or mostly H_2S? **(c)** Calculate the values of K_c and K_p if you rewrote the balanced chemical equation with 1 mol of $H_2(g)$ instead of 2 mol.

15.25 At 1000 K, $K_p = 1.85$ for the reaction

$$SO_2(g) + \tfrac{1}{2} O_2(g) \rightleftharpoons SO_3(g)$$

(a) What is the value of K_p for the reaction $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2} O_2(g)$? **(b)** What is the value of K_p for the reaction $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$? **(c)** What is the value of K_c for the reaction in part (b)?

15.26 Consider the following equilibrium, for which $K_p = 0.0752$ at 480 °C:

$$2\ Cl_2(g) + 2\ H_2O(g) \rightleftharpoons 4\ HCl(g) + O_2(g)$$

(a) What is the value of K_p for the reaction $4\ HCl(g) + O_2(g) \rightleftharpoons 2\ Cl_2(g) + 2\ H_2O(g)$? **(b)** What is the value of K_p for the reaction $Cl_2(g) + H_2O(g) \rightleftharpoons 2\ HCl(g) + \frac{1}{2} O_2(g)$? **(c)** What is the value of K_c for the reaction in part (b)?

15.27 The following equilibria were attained at 823 K:

$$CoO(s) + H_2(g) \rightleftharpoons Co(s) + H_2O(g) \quad K_c = 67$$
$$CoO(s) + CO(g) \rightleftharpoons Co(s) + CO_2(g) \quad K_c = 490$$

Based on these equilibria, calculate the equilibrium constant for $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$ at 823 K.

15.28 Consider the equilibrium

$$N_2(g) + O_2(g) + Br_2(g) \rightleftharpoons 2\ NOBr(g)$$

Calculate the equilibrium constant K_p for this reaction, given the following information (at 298 K):

$$2\ NO(g) + Br_2(g) \rightleftharpoons 2\ NOBr(g) \qquad K_c = 2.0$$
$$2\ NO(g) \rightleftharpoons N_2(g) + O_2(g) \quad K_c = 2.1 \times 10^{30}$$

15.29 Explain why we normally exclude pure solids and liquids from equilibrium-constant expressions.

15.30 Explain why we normally exclude solvents from liquid-phase reactions in equilibrium-constant expressions.

15.31 Mercury(I) oxide decomposes into elemental mercury and elemental oxygen: $2\ Hg_2O(s) \rightleftharpoons 4\ Hg(l) + O_2(g)$. **(a)** Write the equilibrium-constant expression for this reaction in terms of partial pressures. **(b)** Suppose you run this reaction in a solvent that dissolves elemental mercury and elemental oxygen. Rewrite the equilibrium-constant expression in terms of molarities for the reaction, using (solv) to indicate solvation.

15.32 Consider the equilibrium $Na_2O(s) + SO_2(g) \rightleftharpoons Na_2SO_3(s)$. **(a)** Write the equilibrium-constant expression for this reaction in terms of partial pressures. **(b)** All the compounds in this reaction are soluble in water. Rewrite the equilibrium-constant expression in terms of molarities for the aqueous reaction.

CALCULATING EQUILIBRIUM CONSTANTS (section 15.5)

15.33 Methanol (CH_3OH) is produced commercially by the catalyzed reaction of carbon monoxide and hydrogen: $CO(g) + 2\ H_2(g) \rightleftharpoons CH_3OH(g)$. An equilibrium mixture in a 2.00-L vessel is found to contain 0.0406 mol CH_3OH, 0.170 mol CO, and 0.302 mol H_2 at 500 K. Calculate K_c at this temperature.

15.34 Gaseous hydrogen iodide is placed in a closed container at 425 °C, where it partially decomposes to hydrogen and iodine: $2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$. At equilibrium it is found that $[HI] = 3.53 \times 10^{-3}\ M$, $[H_2] = 4.79 \times 10^{-4}\ M$, and $[I_2] = 4.79 \times 10^{-4}\ M$. What is the value of K_c at this temperature?

15.35 The equilibrium $2\ NO(g) + Cl_2(g) \rightleftharpoons 2\ NOCl(g)$ is established at 500 K. An equilibrium mixture of the three gases has partial pressures of 0.095 atm, 0.171 atm, and 0.28 atm for NO, Cl_2, and NOCl, respectively. **(a)** Calculate K_p for this reaction at 500.0 K. **(b)** If the vessel has a volume of 5.00 L, calculate K_c at this temperature.

15.36 Phosphorus trichloride gas and chlorine gas react to form phosphorus pentachloride gas: $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$. A 7.5-L gas vessel is charged with a mixture of $PCl_3(g)$ and $Cl_2(g)$, which is allowed to equilibrate at 450 K. At equilibrium the partial pressures of the three gases are $P_{PCl_3} = 0.124$ atm, $P_{Cl_2} = 0.157$ atm, and $P_{PCl_5} = 1.30$ atm. **(a)** What is the value of K_p at this temperature? **(b)** Does the equilibrium favor reactants or products? **(c)** Calculate K_c for this reaction at 450 K.

15.37 A mixture of 0.10 mol of NO, 0.050 mol of H_2, and 0.10 mol of H_2O is placed in a 1.0-L vessel at 300 K. The following equilibrium is established:

$$2\ NO(g) + 2\ H_2(g) \rightleftharpoons N_2(g) + 2\ H_2O(g)$$

At equilibrium $[NO] = 0.062\ M$. **(a)** Calculate the equilibrium concentrations of H_2, N_2, and H_2O. **(b)** Calculate K_c.

15.38 A mixture of 1.374 g of H_2 and 70.31 g of Br_2 is heated in a 2.00-L vessel at 700 K. These substances react according to

$$H_2(g) + Br_2(g) \rightleftharpoons 2\ HBr(g)$$

At equilibrium the vessel is found to contain 0.566 g of H_2. (**a**) Calculate the equilibrium concentrations of H_2, Br_2, and HBr. (**b**) Calculate K_c.

15.39 A mixture of 0.2000 mol of CO_2, 0.1000 mol of H_2, and 0.1600 mol of H_2O is placed in a 2.000-L vessel. The following equilibrium is established at 500 K:

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

(**a**) Calculate the initial partial pressures of CO_2, H_2, and H_2O. (**b**) At equilibrium $P_{H_2O} = 3.51$ atm. Calculate the equilibrium partial pressures of CO_2, H_2, and CO. (**c**) Calculate K_p for the reaction. (**d**) Calculate K_c for the reaction.

15.40 A flask is charged with 1.500 atm of $N_2O_4(g)$ and 1.00 atm $NO_2(g)$ at 25 °C, and the following equilibrium is achieved:

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$

After equilibrium is reached, the partial pressure of NO_2 is 0.512 atm. (**a**) What is the equilibrium partial pressure of N_2O_4? (**b**) Calculate the value of K_p for the reaction. (**c**) Calculate K_c for the reaction.

15.41 Two different proteins X and Y are dissolved in aqueous solution at 37 °C. The proteins bind in a 1:1 ratio to form XY. A solution that is initially 1.00 mM in each protein is allowed to reach equilibrium. At equilibrium, 0.20 mM of free X and 0.20 mM of free Y remain. What is K_c for the reaction?

[15.42] A chemist at a pharmaceutical company is measuring equilibrium constants for reactions in which drug candidate molecules bind to a protein involved in cancer. The drug molecules bind the protein in a 1:1 ratio to form a drug-protein complex. The protein concentration in aqueous solution at 25 °C is $1.50 \times 10^{-6}\,M$. Drug A is introduced into the protein solution at an initial concentration of $2.00 \times 10^{-6}\,M$. Drug B is introduced into a separate, identical protein solution at an initial concentration of $2.00 \times 10^{-6}\,M$. At equilibrium, the drug A-protein solution has an A-protein complex concentration of $1.00 \times 10^{-6}\,M$, and the drug B solution has a B-protein complex concentration of $1.40 \times 10^{-6}\,M$. Calculate the K_c value for the A-protein binding reaction and for the B-protein binding reaction. Assuming that the drug that binds more strongly will be more effective, which drug is the better choice for further research?

APPLICATIONS OF EQUILIBRIUM CONSTANTS (section 15.6)

15.43 (**a**) How does a reaction quotient differ from an equilibrium constant? (**b**) If $Q_c < K_c$, in which direction will a reaction proceed in order to reach equilibrium? (**c**) What condition must be satisfied so that $Q_c = K_c$?

15.44 (**a**) How is a reaction quotient used to determine whether a system is at equilibrium? (**b**) If $Q_c > K_c$, how must the reaction proceed to reach equilibrium? (**c**) At the start of a certain reaction, only reactants are present; no products have been formed. What is the value of Q_c at this point in the reaction?

15.45 At 100 °C the equilibrium constant for the reaction $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ has the value $K_c = 2.19 \times 10^{-10}$. Are the following mixtures of $COCl_2$, CO, and Cl_2 at 100 °C at equilibrium? If not, indicate the direction that the reaction must proceed to achieve equilibrium. (**a**) $[COCl_2] = 2.00 \times 10^{-3}\,M$, $[CO] = 3.3 \times 10^{-6}\,M$, $[Cl_2] = 6.62 \times 10^{-6}\,M$; (**b**) $[COCl_2] = 4.50 \times 10^{-2}\,M$, $[CO] = 1.1 \times 10^{-7}\,M$, $[Cl_2] = 2.25 \times 10^{-6}\,M$; (**c**) $[COCl_2] = 0.0100\,M$, $[CO] = [Cl_2] = 1.48 \times 10^{-6}\,M$

15.46 As shown in Table 15.2, K_p for the equilibrium

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

is 4.51×10^{-5} at 450 °C. For each of the mixtures listed here, indicate whether the mixture is at equilibrium at 450 °C. If it is not at equilibrium, indicate the direction (toward product or toward reactants) in which the mixture must shift to achieve equilibrium.
(**a**) 98 atm NH_3, 45 atm N_2, 55 atm H_2
(**b**) 57 atm NH_3, 143 atm N_2, no H_2
(**c**) 13 atm NH_3, 27 atm N_2, 82 atm H_2

15.47 At 100 °C, $K_c = 0.078$ for the reaction

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

In an equilibrium mixture of the three gases, the concentrations of SO_2Cl_2 and SO_2 are 0.108 M and 0.052 M, respectively. What is the partial pressure of Cl_2 in the equilibrium mixture?

15.48 At 900 K the following reaction has $K_p = 0.345$:

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

In an equilibrium mixture the partial pressures of SO_2 and O_2 are 0.135 atm and 0.455 atm, respectively. What is the equilibrium partial pressure of SO_3 in the mixture?

15.49 (**a**) At 1285 °C the equilibrium constant for the reaction $Br_2(g) \rightleftharpoons 2\,Br(g)$ is $K_c = 1.04 \times 10^{-3}$. A 0.200-L vessel containing an equilibrium mixture of the gases has 0.245 g $Br_2(g)$ in it. What is the mass of Br(g) in the vessel? (**b**) For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, $K_c = 55.3$ at 700 K. In a 2.00-L flask containing an equilibrium mixture of the three gases, there are 0.056 g H_2 and 4.36 g I_2. What is the mass of HI in the flask?

15.50 (**a**) At 800 K the equilibrium constant for $I_2(g) \rightleftharpoons 2\,I(g)$ is $K_c = 3.1 \times 10^{-5}$. If an equilibrium mixture in a 10.0-L vessel contains 2.67×10^{-2} g of I(g), how many grams of I_2 are in the mixture? (**b**) For $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$, $K_p = 3.0 \times 10^4$ at 700 K. In a 2.00-L vessel the equilibrium mixture contains 1.17 g of SO_3 and 0.105 g of O_2. How many grams of SO_2 are in the vessel?

15.51 At 2000 °C the equilibrium constant for the reaction

$$2\,NO(g) \rightleftharpoons N_2(g) + O_2(g)$$

is $K_c = 2.4 \times 10^3$. If the initial concentration of NO is 0.175 M, what are the equilibrium concentrations of NO, N_2, and O_2?

15.52 For the equilibrium

$$Br_2(g) + Cl_2(g) \rightleftharpoons 2\,BrCl(g)$$

at 400 K, $K_c = 7.0$. If 0.25 mol of Br_2 and 0.55 mol of Cl_2 are introduced into a 3.0-L container at 400 K, what will be the equilibrium concentrations of Br_2, Cl_2, and BrCl?

15.53 At 373 K, $K_p = 0.416$ for the equilibrium

$$2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g)$$

If the pressures of NOBr(g) and NO(g) are equal, what is the equilibrium pressure of $Br_2(g)$?

15.54 At 218 °C, $K_c = 1.2 \times 10^{-4}$ for the equilibrium

$$NH_4SH(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

Calculate the equilibrium concentrations of NH_3 and H_2S if a sample of solid NH_4SH is placed in a closed vessel at 218 °C and decomposes until equilibrium is reached.

15.55 Consider the reaction

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

At 25 °C the equilibrium constant is $K_c = 2.4 \times 10^{-5}$ for this reaction. **(a)** If excess $CaSO_4(s)$ is mixed with water at 25 °C to produce a saturated solution of $CaSO_4$, what are the equilibrium concentrations of Ca^{2+} and SO_4^{2-}? **(b)** If the resulting solution has a volume of 1.4 L, what is the minimum mass of $CaSO_4(s)$ needed to achieve equilibrium?

15.56 At 80 °C, $K_c = 1.87 \times 10^{-3}$ for the reaction

$$PH_3BCl_3(s) \rightleftharpoons PH_3(g) + BCl_3(g)$$

(a) Calculate the equilibrium concentrations of PH_3 and BCl_3 if a solid sample of PH_3BCl_3 is placed in a closed vessel at 80 °C and decomposes until equilibrium is reached. **(b)** If the flask has a volume of 0.250 L, what is the minimum mass of $PH_3BCl_3(s)$ that must be added to the flask to achieve equilibrium?

15.57 For the reaction $I_2 + Br_2(g) \rightleftharpoons 2\,IBr(g)$, $K_c = 280$ at 150 °C. Suppose that 0.500 mol IBr in a 2.00-L flask is allowed to reach equilibrium at 150 °C. What are the equilibrium concentrations of IBr, I_2, and Br_2?

15.58 At 25 °C the reaction

$$CaCrO_4(s) \rightleftharpoons Ca^{2+}(aq) + CrO_4^{2-}(aq)$$

has an equilibrium constant $K_c = 7.1 \times 10^{-4}$. What are the equilibrium concentrations of Ca^{2+} and CrO_4^{2-} in a saturated solution of $CaCrO_4$?

15.59 Methane, CH_4, reacts with I_2 according to the reaction $CH_4(g) + I_2(g) \rightleftharpoons CH_3I(g) + HI(g)$. At 630 K, K_p for this reaction is 2.26×10^{-4}. A reaction was set up at 630 K with initial partial pressures of methane of 105.1 torr and of 7.96 torr for I_2. Calculate the pressures, in torr, of all reactants and products at equilibrium.

15.60 The reaction of an organic acid with an alcohol, in organic solvent, to produce an ester and water is commonly done in the pharmaceutical industry. This reaction is catalyzed by strong acid (usually H_2SO_4). A simple example is the reaction of acetic acid with ethyl alcohol to produce ethyl acetate and water:

$$CH_3COOH(solv) + CH_3CH_2OH(solv) \rightleftharpoons CH_3COOCH_2CH_3(solv) + H_2O(solv)$$

where "(*solv*)" indicates that all reactants and products are in solution but not an aqueous solution. The equilibrium constant for this reaction at 55 °C is 6.68. A pharmaceutical chemist makes up 15.0 L of a solution that is initially 0.275 *M* in acetic acid and 3.85 *M* in ethanol. At equilibrium, how many grams of ethyl acetate are formed?

LE CHÂTELIER'S PRINCIPLE (section 15.7)

15.61 Consider the following equilibrium for which $\Delta H < 0$

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

How will each of the following changes affect an equilibrium mixture of the three gases: **(a)** $O_2(g)$ is added to the system; **(b)** the reaction mixture is heated; **(c)** the volume of the reaction vessel is doubled; **(d)** a catalyst is added to the mixture; **(e)** the total pressure of the system is increased by adding a noble gas; **(f)** $SO_3(g)$ is removed from the system?

15.62 Consider $4\,NH_3(g) + 5\,O_2(g) \rightleftharpoons 4\,NO(g) + 6\,H_2O(g)$, $\Delta H = -904.4$ kJ. How does each of the following changes affect the yield of NO at equilibrium? Answer increase, decrease, or no change: **(a)** increase $[NH_3]$; **(b)** increase $[H_2O]$; **(c)** decrease $[O_2]$; **(d)** decrease the volume of the container in which the reaction occurs; **(e)** add a catalyst; **(f)** increase temperature.

15.63 How do the following changes affect the value of the equilibrium constant for a gas-phase exothermic reaction: **(a)** removal of a reactant **(b)** removal of a product, **(c)** decrease in the volume, **(d)** decrease in the temperature, **(e)** addition of a catalyst?

15.64 For a certain gas-phase reaction, the fraction of products in an equilibrium mixture is increased by either increasing the temperature or by increasing the volume of the reaction vessel. **(a)** Is the reaction exothermic or endothermic? **(b)** Does the balanced chemical equation have more molecules on the reactant side or product side?

15.65 Consider the following equilibrium between oxides of nitrogen

$$3\,NO(g) \rightleftharpoons NO_2(g) + N_2O(g)$$

(a) Use data in Appendix C to calculate $\Delta H°$ for this reaction. **(b)** Will the equilibrium constant for the reaction increase or decrease with increasing temperature? Explain. **(c)** At constant temperature, would a change in the volume of the container affect the fraction of products in the equilibrium mixture?

15.66 Methanol (CH_3OH) can be made by the reaction of CO with H_2:

$$CO(g) + 2\,H_2(g) \rightleftharpoons CH_3OH(g)$$

(a) Use thermochemical data in Appendix C to calculate $\Delta H°$ for this reaction. **(b)** To maximize the equilibrium yield of methanol, would you use a high or low temperature? **(c)** To maximize the equilibrium yield of methanol, would you use a high or low pressure?

15.67 Ozone, O_3, decomposes to molecular oxygen in the stratosphere according to the reaction $2\,O_3(g) \rightarrow 3\,O_2(g)$. Would an increase in pressure favor the formation of ozone or of oxygen?

15.68 *Bioremediation* is the use of microorganisms to degrade environmental pollutants. Many pollutants contain only carbon and hydrogen (oil being one example). The chemical reactions are complicated, but in general the microorganisms react the pollutant hydrocarbon with O_2 to produce CO_2 and other carbon-containing compounds that are incorporated into the organism's biomass. How would increasing levels of CO_2 in the environment affect the bioremediation reaction?

ADDITIONAL EXERCISES

15.69 Both the forward reaction and the reverse reaction in the following equilibrium are believed to be elementary steps:

$$CO(g) + Cl_2(g) \rightleftharpoons COCl(g) + Cl(g)$$

At 25 °C the rate constants for the forward and reverse reactions are $1.4 \times 10^{-28}\ M^{-1}\ s^{-1}$ and $9.3 \times 10^{10}\ M^{-1}\ s^{-1}$, respectively. **(a)** What is the value for the equilibrium constant at 25 °C? **(b)** Are reactants or products more plentiful at equilibrium? **(c)** What additional information would you need in order to decide whether the reaction as written is endothermic or exothermic?

15.70 If $K_c = 1$ for the equilibrium $2\ A(g) \rightleftharpoons B(g)$, what is the relationship between [A] and [B] at equilibrium?

15.71 A mixture of CH_4 and H_2O is passed over a nickel catalyst at 1000 K. The emerging gas is collected in a 5.00-L flask and is found to contain 8.62 g of CO, 2.60 g of H_2, 43.0 g of CH_4, and 48.4 g of H_2O. Assuming that equilibrium has been reached, calculate K_c and K_p for the reaction.

15.72 When 2.00 mol of SO_2Cl_2 is placed in a 2.00-L flask at 303 K, 56% of the SO_2Cl_2 decomposes to SO_2 and Cl_2:

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

(a) Calculate K_c for this reaction at this temperature. **(b)** Calculate K_p for this reaction at 303 K. **(c)** Repeat these calculations for 2.00 mol of SO_2Cl_2 in a 15.00-L vessel at 303 K.

15.73 A mixture of H_2, S, and H_2S is held in a 1.0-L vessel at 90 °C and reacts according to the equation:

$$H_2(g) + S(s) \rightleftharpoons H_2S(g)$$

At equilibrium the mixture contains 0.46 g of H_2S and 0.40 g H_2. **(a)** Write the equilibrium-constant expression for this reaction. **(b)** What is the value of K_c for the reaction at this temperature? **(c)** Why can we ignore the amount of S when doing the calculation in part (b)?

15.74 A sample of nitrosyl bromide (NOBr) decomposes according to the equation

$$2\ NOBr(g) \rightleftharpoons 2\ NO(g) + Br_2(g)$$

An equilibrium mixture in a 5.00-L vessel at 100 °C contains 3.22 g of NOBr, 3.08 g of NO, and 4.19 g of Br_2. **(a)** Calculate K_c. **(b)** What is the total pressure exerted by the mixture of gases? **(c)** What was the mass of the original sample of NOBr?

15.75 Consider the hypothetical reaction $A(g) \rightleftharpoons 2\ B(g)$. A flask is charged with 0.75 atm of pure A, after which it is allowed to reach equilibrium at 0 °C. At equilibrium the partial pressure of A is 0.36 atm. **(a)** What is the total pressure in the flask at equilibrium? **(b)** What is the value of K_p? **(c)** What could we do to maximize the yield of B?

15.76 As shown in Table 15.2, the equilibrium constant for the reaction $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$ is $K_p = 4.34 \times 10^{-3}$ at 300 °C. Pure NH_3 is placed in a 1.00-L flask and allowed to reach equilibrium at this temperature. There are 1.05 g NH_3 in the equilibrium mixture. **(a)** What are the masses of N_2 and H_2 in the equilibrium mixture? **(b)** What was the initial mass of ammonia placed in the vessel? **(c)** What is the total pressure in the vessel?

15.77 For the equilibrium

$$2\ IBr(g) \rightleftharpoons I_2(g) + Br_2(g)$$

$K_p = 8.5 \times 10^{-3}$ at 150 °C. If 0.025 atm of IBr is placed in a 2.0-L container, what is the partial pressure of all substances after equilibrium is reached?

15.78 For the equilibrium

$$PH_3BCl_3(s) \rightleftharpoons PH_3(g) + BCl_3(g)$$

$K_p = 0.052$ at 60 °C. **(a)** Calculate K_c. **(b)** After 3.00 g of solid PH_3BCl_3 is added to a closed 1.500-L vessel at 60 °C, the vessel is charged with 0.0500 g of $BCl_3(g)$. What is the equilibrium concentration of PH_3?

[15.79] Solid NH_4SH is introduced into an evacuated flask at 24 °C. The following reaction takes place:

$$NH_4SH(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

At equilibrium the total pressure (for NH_3 and H_2S taken together) is 0.614 atm. What is K_p for this equilibrium at 24 °C?

[15.80] A 0.831-g sample of SO_3 is placed in a 1.00-L container and heated to 1100 K. The SO_3 decomposes to SO_2 and O_2:

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

At equilibrium the total pressure in the container is 1.300 atm. Find the values of K_p and K_c for this reaction at 1100 K.

15.81 Nitric oxide (NO) reacts readily with chlorine gas as follows:

$$2\ NO(g) + Cl_2(g) \rightleftharpoons 2\ NOCl(g)$$

At 700 K the equilibrium constant K_p for this reaction is 0.26. Predict the behavior of each of the following mixtures at this temperature and indicate whether or not the mixtures are at equilibrium. If not, state whether the mixture will need to produce more products or reactants to reach equilibrium. **(a)** $P_{NO} = 0.15$ atm, $P_{Cl_2} = 0.31$ atm, and $P_{NOCl} = 0.11$ atm; **(b)** $P_{NO} = 0.12$ atm, $P_{Cl_2} = 0.10$ atm, and $P_{NOCl} = 0.050$ atm; **(c)** $P_{NO} = 0.15$ atm, $P_{Cl_2} = 0.20$ atm, and $P_{NOCl} = 5.10 \times 10^{-3}$ atm.

15.82 At 900 °C, $K_c = 0.0108$ for the reaction

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

A mixture of $CaCO_3$, CaO, and CO_2 is placed in a 10.0-L vessel at 900 °C. For the following mixtures, will the amount of $CaCO_3$ increase, decrease, or remain the same as the system approaches equilibrium?

(a) 15.0 g $CaCO_3$, 15.0 g CaO, and 4.25 g CO_2
(b) 2.50 g $CaCO_3$, 25.0 g CaO, and 5.66 g CO_2
(c) 30.5 g $CaCO_3$, 25.5 g CaO, and 6.48 g CO_2

15.83 When 1.50 mol CO_2 and 1.50 mol H_2 are placed in a 3.00-L container at 395 °C, the following reaction occurs: $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$. If $K_c = 0.802$, what are the concentrations of each substance in the equilibrium mixture?

15.84 The equilibrium constant K_c for $C(s) + CO_2(g) \rightleftharpoons 2\ CO(g)$ is 1.9 at 1000 K and 0.133 at 298 K. **(a)** If excess C is allowed to react with 25.0 g of CO_2 in a 3.00-L vessel at 1000 K, how many grams of CO are produced? **(b)** How many grams of C are consumed? **(c)** If a smaller vessel is used for the reaction, will the yield of CO be greater or smaller? **(d)** Is the reaction endothermic or exothermic?

15.85 NiO is to be reduced to nickel metal in an industrial process by use of the reaction

$$NiO(s) + CO(g) \rightleftharpoons Ni(s) + CO_2(g)$$

At 1600 K the equilibrium constant for the reaction is $K_p = 6.0 \times 10^2$. If a CO pressure of 150 torr is to be employed in the furnace and total pressure never exceeds 760 torr, will reduction occur?

15.86 Le Châtelier noted that many industrial processes of his time could be improved by an understanding of chemical equilibria. For example, the reaction of iron oxide with carbon monoxide was used to produce elemental iron and CO_2 according to the reaction

$$Fe_2O_3(s) + 3\,CO(g) \rightleftharpoons 2\,Fe(s) + 3\,CO_2(g)$$

Even in Le Châtelier's time, it was noted that a great deal of CO was wasted, expelled through the chimneys over the furnaces. Le Châtelier wrote, "Because this incomplete reaction was thought to be due to an insufficiently prolonged contact between carbon monoxide and the iron ore [oxide], the dimensions of the furnaces have been increased. In England they have been made as high as thirty meters. But the proportion of carbon monoxide escaping has not diminished, thus demonstrating, by an experiment costing several hundred thousand francs, that the reduction of iron oxide by carbon monoxide is a limited reaction. Acquaintance with the laws of chemical equilibrium would have permitted the same conclusion to be reached more rapidly and far more economically." What does this anecdote tell us about the equilibrium constant for this reaction?

[15.87] At 700 K the equilibrium constant for the reaction

$$CCl_4(g) \rightleftharpoons C(s) + 2\,Cl_2(g)$$

is $K_p = 0.76$. A flask is charged with 2.00 atm of CCl_4, which then reaches equilibrium at 700 K. **(a)** What fraction of the CCl_4 is converted into C and Cl_2? **(b)** What are the partial pressures of CCl_4 and Cl_2 at equilibrium?

[15.88] The reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ has $K_p = 0.0870$ at 300 °C. A flask is charged with 0.50 atm PCl_3, 0.50 atm Cl_2, and 0.20 atm PCl_5 at this temperature. **(a)** Use the reaction quotient to determine the direction the reaction must proceed to reach equilibrium. **(b)** Calculate the equilibrium partial pressures of the gases. **(c)** What effect will increasing the volume of the system have on the mole fraction of Cl_2 in the equilibrium mixture? **(d)** The reaction is exothermic. What effect will increasing the temperature of the system have on the mole fraction of Cl_2 in the equilibrium mixture?

[15.89] An equilibrium mixture of H_2, I_2, and HI at 458 °C contains 0.112 mol H_2, 0.112 mol I_2, and 0.775 mol HI in a 5.00-L vessel. What are the equilibrium partial pressures when equilibrium is reestablished following the addition of 0.200 mol of HI?

[15.90] Consider the hypothetical reaction $A(g) + 2\,B(g) \rightleftharpoons 2\,C(g)$, for which $K_c = 0.25$ at a certain temperature. A 1.00-L reaction vessel is loaded with 1.00 mol of compound C, which is allowed to reach equilibrium. Let the variable x represent the number of mol/L of compound A present at equilibrium. **(a)** In terms of x, what are the equilibrium concentrations of compounds B and C? **(b)** What limits must be placed on the value of x so that all concentrations are positive? **(c)** By putting the equilibrium concentrations (in terms of x) into the equilibrium-constant expression, derive an equation that can be solved for x. **(d)** The equation from part (c) is a cubic equation (one that has the form $ax^3 + bx^2 + cx + d = 0$). In general, cubic equations cannot be solved in closed form. However, you can estimate the solution by plotting the cubic equation in the allowed range of x that you specified in part (b). The point at which the cubic equation crosses the x-axis is the solution. **(e)** From the plot in part (d), estimate the equilibrium concentrations of A, B, and C. (*Hint:* You can check the accuracy of your answer by substituting these concentrations into the equilibrium expression.)

15.91 At 1200 K, the approximate temperature of automobile exhaust gases (Figure 15.15), K_p for the reaction

$$2\,CO_2(g) \rightleftharpoons 2\,CO(g) + O_2(g)$$

is about 1×10^{-13}. Assuming that the exhaust gas (total pressure 1 atm) contains 0.2% CO, 12% CO_2, and 3% O_2 by volume, is the system at equilibrium with respect to the CO_2 reaction? Based on your conclusion, would the CO concentration in the exhaust be decreased or increased by a catalyst that speeds up the CO_2 reaction?

15.92 Suppose that you worked at the U.S. Patent Office and a patent application came across your desk claiming that a newly developed catalyst was much superior to the Haber catalyst for ammonia synthesis because the catalyst led to much greater equilibrium conversion of N_2 and H_2 into NH_3 than the Haber catalyst under the same conditions. What would be your response?

INTEGRATIVE EXERCISES

15.93 Consider the reaction $IO_4^-(aq) + 2\,H_2O(l) \rightleftharpoons H_4IO_6^-(aq)$; $K_c = 3.5 \times 10^{-2}$. If you start with 25.0 mL of a 0.905 *M* solution of $NaIO_4$, and then dilute it with water to 500.0 mL, what is the concentration of $H_4IO_6^-$ at equilibrium?

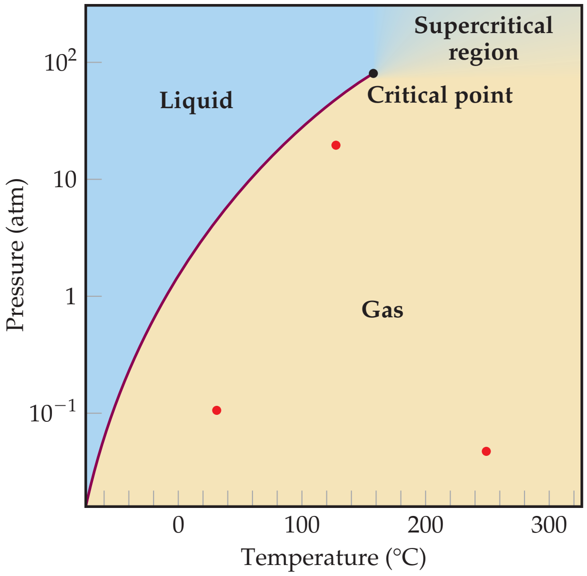
[15.94] Silver chloride, AgCl(*s*), is an "insoluble" strong electrolyte. **(a)** Write the equation for the dissolution of AgCl(*s*) in $H_2O(l)$. **(b)** Write the expression for K_c for the reaction in part (a). **(c)** Based on the thermochemical data in Appendix C and Le Châtelier's principle, predict whether the solubility of AgCl in H_2O increases or decreases with increasing temperature. **(d)** The equilibrium constant for the dissolution of AgCl in water is 1.6×10^{-10} at 25 °C. In addition, $Ag^+(aq)$ can react with $Cl^-(aq)$ according to the reaction

$$Ag^+(aq) + 2\,Cl^-(aq) \longrightarrow AgCl_2^-(aq)$$

where $K_c = 1.8 \times 10^5$ at 25 °C. Although AgCl is "not soluble" in water, the complex $AgCl_2^-$ is soluble. At 25 °C, is the solubility of AgCl in a 0.100 *M* NaCl solution *greater* than the solubility of AgCl in pure water, due to the formation of soluble $AgCl_2^-$ ions? Or is the AgCl solubility in 0.100 *M* NaCl *less* than in pure water because of a Le Châtelier–type argument? Justify your answer with calculations. (*Hint*: Any form in which silver is in solution counts as "solubility.")

[15.95] Consider the equilibrium $A \rightleftharpoons B$ in which both the forward and reverse reactions are elementary (single-step) reactions. Assume that the only effect of a catalyst on the reaction is to lower the activation energies of the forward and reverse reactions, as shown in Figure 15.14. Using the Arrhenius equation (Section 14.5), prove that the equilibrium constant is the same for the catalyzed reaction as for the uncatalyzed one.

[15.96] The phase diagram for SO_2 is shown here. (**a**) What does this diagram tell you about the enthalpy change in the reaction $SO_2(l) \longrightarrow SO_2(g)$? (**b**) Calculate the equilibrium constant for this reaction at 100 °C and at 0 °C. (**c**) Why is it not possible to calculate an equilibrium constant between the gas and liquid phases in the supercritical region? (**d**) At which of the three points marked in red does $SO_2(g)$ most closely approach ideal-gas behavior? (**e**) At which of the three red points does $SO_2(g)$ behave least ideally?



[15.97] Write the equilibrium-constant expression for the equilibrium

$$C(s) + CO_2(g) \rightleftharpoons 2\,CO(g)$$

The table that follows shows the relative mole percentages of $CO_2(g)$ and $CO(g)$ at a total pressure of 1 atm for several temperatures. Calculate the value of K_p at each temperature. Is the reaction exothermic or endothermic? Explain.

Temperature (°C)	CO_2 (mol %)	CO (mol %)
850	6.23	93.77
950	1.32	98.68
1050	0.37	99.63
1200	0.06	99.94

15.98 In Section 11.5 we defined the vapor pressure of a liquid in terms of an equilibrium. (**a**) Write the equation representing the equilibrium between liquid water and water vapor and the corresponding expression for K_p. (**b**) By using data in Appendix B, give the value of K_p for this reaction at 30 °C. (**c**) What is the value of K_p for any liquid in equilibrium with its vapor at the normal boiling point of the liquid?

15.99 Water molecules in the atmosphere can form hydrogen-bonded dimers, $(H_2O)_2$. The presence of these dimers is thought to be important in the nucleation of ice crystals in the atmosphere and in the formation of acid rain. (**a**) Using VSEPR theory, draw the structure of a water dimer, using dashed lines to indicate intermolecular interactions. (**b**) What kind of intermolecular forces are involved in water dimer formation? (**c**) The K_p for water dimer formation in the gas phase is 0.050 at 300 K and 0.020 at 350 K. Is water dimer formation endothermic or exothermic?

15.100 The protein hemoglobin (Hb) transports O_2 in mammalian blood. Each Hb can bind 4 O_2 molecules. The equilibrium constant for the O_2-binding reaction is higher in fetal hemoglobin than in adult hemoglobin. In discussing protein oxygen-binding capacity, biochemists use a measure called the *P50 value*, defined as the partial pressure of oxygen at which 50% of the protein is saturated. Fetal hemoglobin has a P50 value of 19 torr, and adult hemoglobin has a P50 value of 26.8 torr. Use these data to estimate how much larger K_c is for the aqueous reaction $4\,O_2(g) + Hb(aq) \longrightarrow [Hb(O_2)_4(aq)]$.