

# 15

## CHEMICAL EQUILIBRIUM

### 15.1 | The Concept of 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*, whereby a forward process and the reverse process take place at the same rate so that no net change occurs. Team sports that allow player substitutions (rugby, water polo, and soccer for example) are examples of *dynamic* equilibria. The number of players ‘in play’ is always constant, but they are not always the same players because of the substitutions that are allowed,

### WHAT'S AHEAD

- 15.1 ► The Concept of Equilibrium
- 15.2 ► The Equilibrium Constant
- 15.3 ► Understanding and Working with Equilibrium Constants
- 15.4 ► Calculating Equilibrium Constants
- 15.5 ► Le Châtelier’s Principle

We have already encountered several examples of dynamic equilibrium involving physical changes of matter, including vapor pressure, the formation of saturated solutions, and Henry's law. Consider vapor pressure as an illustrative example. In a closed container, the pressure of a vapor above a liquid stops changing when the rate at which molecules escaping from the liquid into the gas phase equals the rate at which molecules from the gas phase are captured by and reenter the liquid.

Just like evaporation and condensation, or dissolution and crystallization, chemical reactions can run in the forward and reverse directions. If the reverse reaction is sufficiently slow, we can neglect it altogether, as we have done in reactions we've encountered up to this point, but there are many important examples where we must consider the rates of both forward and reverse reactions.

***Chemical equilibrium occurs when the forward and reverse reactions proceed at equal rates.***

When a reaction is at equilibrium, 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, and the reaction appears to stop before it reaches completion.

In this and the next two chapters, we will explore chemical equilibrium in 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.

At the end of this section, you should be able to

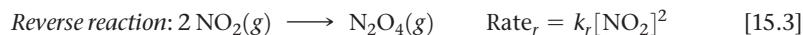
- Explain what is meant by chemical equilibrium and how it relates to reaction rates

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  $\text{N}_2\text{O}_4$ , a colorless substance that dissociates to form brown  $\text{NO}_2$ . **Figure 15.1** shows a sample of frozen  $\text{N}_2\text{O}_4$  inside a sealed tube. The solid  $\text{N}_2\text{O}_4$  becomes a gas as it is warmed above its boiling point ( $21.2^\circ\text{C}$ ), and the gas turns darker as the colorless  $\text{N}_2\text{O}_4$  gas dissociates into brown  $\text{NO}_2$  gas. Eventually, even though there is still  $\text{N}_2\text{O}_4$  in the tube, the color stops getting darker because the system reaches equilibrium. We are left with an *equilibrium mixture* of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  in which the concentrations of the gases no longer change as time passes. Because the reaction is in a closed system, no gases escape, and the equilibrium mixture can be maintained.

The equilibrium mixture results because the reaction is *reversible*:  $\text{N}_2\text{O}_4$  can form  $\text{NO}_2$ , and  $\text{NO}_2$  can form  $\text{N}_2\text{O}_4$ . Dynamic equilibrium is represented by writing the equation for the reaction with two half arrows pointing in opposite directions:



We can analyze this equilibrium using our knowledge of kinetics. Let's call the decomposition of  $\text{N}_2\text{O}_4$  the forward reaction and the formation of  $\text{N}_2\text{O}_4$  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:



At equilibrium, the rate at which  $\text{NO}_2$  forms in the forward reaction equals the rate at which  $\text{N}_2\text{O}_4$  forms in the reverse reaction:

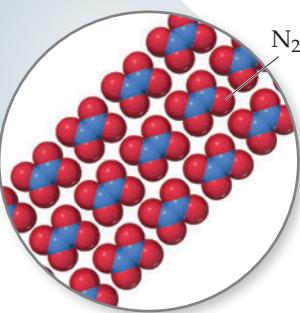
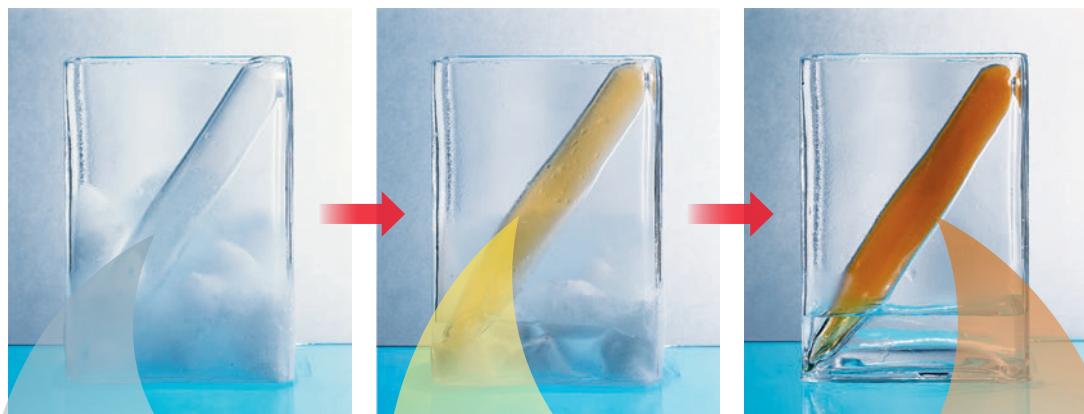
$$\frac{k_f[\text{N}_2\text{O}_4]}{\text{Forward reaction}} = \frac{k_r[\text{NO}_2]^2}{\text{Reverse reaction}} \quad [15.4]$$

Rearranging this equation gives

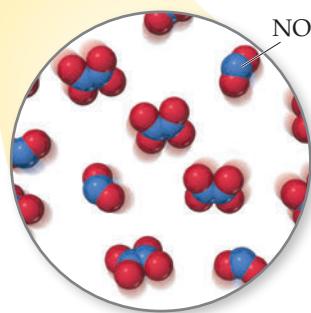
$$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{k_f}{k_r} = \text{a constant} \quad [15.5]$$

 Go Figure

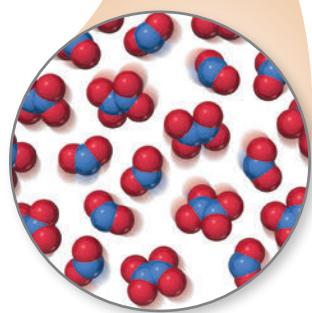
If you were to let the tube on the right sit overnight and then take another picture, would the brown color look darker, lighter, or the same?



Frozen  $\text{N}_2\text{O}_4$  sample is nearly colorless.



On warming, the  $\text{N}_2\text{O}_4$  becomes a gas and partially dissociates to form brown  $\text{NO}_2(g)$ .



Colors stop changing when equilibrium is reached: rate of forward reaction  $\text{N}_2\text{O}_4(g) \rightarrow 2 \text{NO}_2(g)$  = rate of reverse reaction  $2 \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$ .



▲ Figure 15.1 The equilibrium between  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ .

From Equation 15.5, we see that the quotient of two rate constants is another constant, which as we will learn is called the equilibrium constant. We also see that, at equilibrium, the ratio of the concentration terms equals this same constant. It makes no difference whether we start with  $\text{N}_2\text{O}_4$  or with  $\text{NO}_2$ , 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  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  at equilibrium.

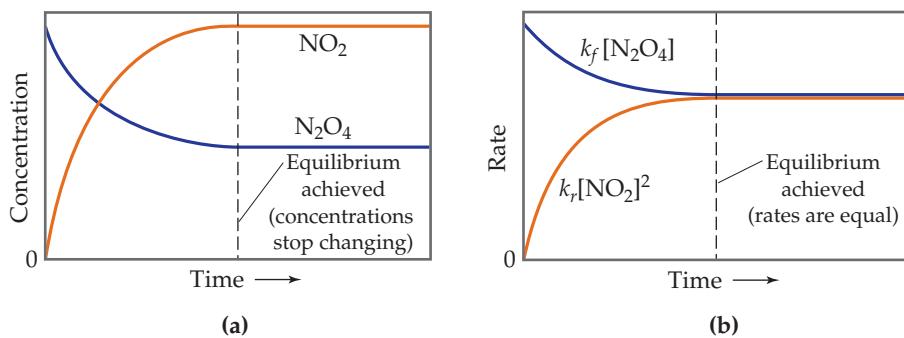
Once equilibrium is established, the concentrations of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  no longer change, as shown in Figure 15.2(a). However, the fact that the composition of the equilibrium mixture remains constant with time does not mean that  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  stop reacting. On the contrary, the equilibrium is *dynamic*—which means some  $\text{N}_2\text{O}_4$  is always converting to  $\text{NO}_2$  and some  $\text{NO}_2$  is always converting to  $\text{N}_2\text{O}_4$ . 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

Why does the rate of the forward reaction slow down as the reaction proceeds?



▲ **Figure 15.2** Achieving chemical equilibrium in the  $\text{N}_2\text{O}_4(\text{g}) \longrightarrow 2 \text{NO}_2(\text{g})$  reaction. Equilibrium occurs when the rate of the forward reaction equals the rate of the reverse reaction.

## Self-Assessment Exercise

- 15.1** Which of the following variables are equal when the  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$  reaction reaches equilibrium?

- (a)  $k_f$  and  $k_r$   
 (b) the forward and reverse reaction rates  
 (c) the concentrations of  $[\text{N}_2\text{O}_4]$  and  $[\text{NO}_2]$

## Exercise

- 15.2** Suppose that the gas-phase reactions  $A \longrightarrow B$  and  $B \longrightarrow A$  are both elementary processes with rate constants of  $2.5 \times 10^{-2} \text{ min}^{-1}$  and  $2.5 \times 10^{-1} \text{ min}^{-1}$ , respectively.

- (a) What is the value of the equilibrium constant for the equilibrium  $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g})$ ? (b) Which is greater at equilibrium, the partial pressure of A or the partial pressure of B?

15.1 (b)

Answers to Self-Assessment Exercise

## 15.2 | The Equilibrium Constant

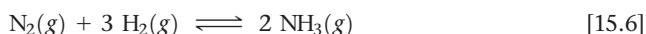


Imagine yourself as a research chemist synthesizing a compound in the laboratory. Before you start a synthesis you need to consider the stoichiometry of the reaction you are undertaking to determine how much of each chemical you need, what solvent would be appropriate to use as well as the rate at which the reaction occurs and whether you will need to employ heat or add a catalyst. In addition, you might have to consider if the reaction is an equilibrium and how that will affect the yield of your desired product.

In this section, we see that equilibria can be quantified. By the end of this section, you should be able to

- Write the equilibrium expression for any reaction
- Convert  $K_c$  to  $K_p$  and vice versa.

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:



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,  $\text{N}_2$  and  $\text{H}_2$  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  $\text{N}_2$  and  $\text{H}_2$ . 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  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{NH}_3$  vary with time is shown in **Figure 15.3**. Notice that an equilibrium mixture is obtained regardless of whether we begin with  $\text{N}_2$  and  $\text{H}_2$  or with  $\text{NH}_3$ . *The equilibrium condition is reached from either direction.*

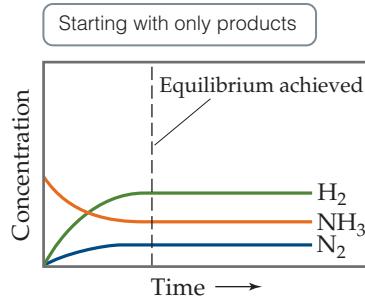
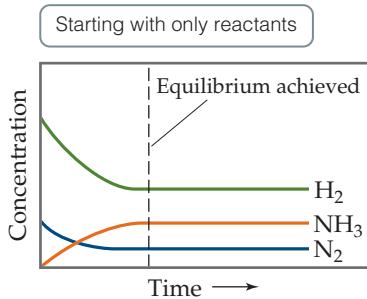
An expression similar to Equation 15.5 governs the concentrations of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  at equilibrium. If we were to systematically change the relative amounts of the three gases in the starting mixture and then analyze each equilibrium mixture, we could determine the 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



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

**Go Figure** Is the rate of disappearance of  $\text{H}_2$  related to the rate of disappearance of  $\text{N}_2$ ? If so, how they are related?



▲ **Figure 15.3** The same equilibrium is reached whether we start with only reactants ( $\text{N}_2$  and  $\text{H}_2$ ) or with only product ( $\text{NH}_3$ ).

$$K_c = \frac{[D]^d [E]^e}{[A]^a [B]^b} \quad \begin{matrix} \longleftarrow & \text{products} \\ \longleftarrow & \text{reactants} \end{matrix} \quad [15.8]$$

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

The numerator of the equilibrium 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,  $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$ , the equilibrium expression is

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \quad [15.9]$$

Once we know the balanced chemical equation for a reaction that reaches equilibrium, we can write the equilibrium expression even if we do not know the reaction mechanism.

*The equilibrium expression depends only on the stoichiometry of the reaction, not on its mechanism.*

In this way equilibrium expressions are different from rate laws.

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.

## 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. 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 (Figure 15.4). The engineering needed to implement the Haber process requires the use of temperatures (approximately 500 °C) and pressures (20 to 60 MPa) 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 perhaps a year earlier 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 180 million tonnes of ammonia are manufactured annually worldwide, mostly by the Haber process. The ammonia can be applied directly to the soil, 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:** 15.21, 15.85



▲ **Figure 15.4** A high-pressure steel reactor used in the Haber process is on display at Karlsruhe Institute of Technology in Germany where the Haber process was developed.



## Sample Exercise 15.1

### Writing Equilibrium Expressions

Write the equilibrium expression for  $K_c$  for the following reactions:

- $2 \text{O}_3(g) \rightleftharpoons 3 \text{O}_2(g)$
- $2 \text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{NOCl}(g)$
- $\text{Ag}^+(aq) + 2 \text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$

### SOLUTION

**Analyze** We are given three equations and are asked to write an equilibrium 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

$$\text{(a)} K_c = \frac{[\text{O}_2]^3}{[\text{O}_3]^2} \quad \text{(b)} K_c = \frac{[\text{NOCl}]^2}{[\text{NO}]^2[\text{Cl}_2]} \quad \text{(c)} K_c = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

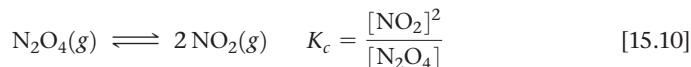
### ► Practice Exercise

For the reaction  $2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g)$ , which of the following is the correct equilibrium expression?

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

## 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:



We start with several sealed tubes containing different concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ . The tubes are kept at  $100^\circ\text{C}$  until equilibrium is reached. We then analyze the mixtures and determine the equilibrium concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ , 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,  $[\text{NO}_2] = 0.0172 \text{ M}$  and  $[\text{N}_2\text{O}_4] = 0.00140 \text{ M}$ , we find

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{[0.0172]^2}{0.00140} = 0.211$$

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, as do the final concentrations.

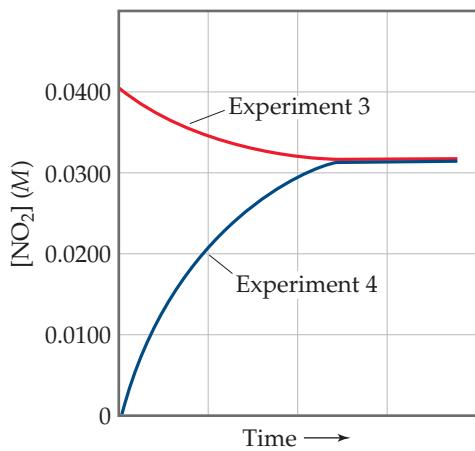
**TABLE 15.1 Initial and Equilibrium Concentrations of  $\text{N}_2\text{O}_4(g)$  and  $\text{NO}_2(g)$  at  $100^\circ\text{C}$**

Experiment	Initial $[\text{N}_2\text{O}_4] (\text{M})$	Initial $[\text{NO}_2] (\text{M})$	Equilibrium $[\text{N}_2\text{O}_4] (\text{M})$	Equilibrium $[\text{NO}_2] (\text{M})$	$K_c$
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



### Go Figure

In which experiment, 3 or 4, does the concentration of  $\text{N}_2\text{O}_4$  decrease to reach equilibrium?



**▲ Figure 15.5** The same equilibrium mixture is produced regardless of the initial  $\text{NO}_2$  concentration. The concentration of  $\text{NO}_2$  either increases or decreases until equilibrium is reached.

Furthermore, Experiment 4 shows that equilibrium can be achieved beginning with  $\text{N}_2\text{O}_4$  rather than with  $\text{NO}_2$ . 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  $\text{NO}_2$  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.

### Equilibrium Constants in Terms of Pressure, $K_p$

When the reactants and products in a chemical reaction are gases, we can formulate the equilibrium 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

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

where  $P_A$  is the partial pressure of A,  $P_B$  is the partial pressure of B, and so forth. For example, for our  $\text{N}_2\text{O}_4/\text{NO}_2$  reaction, we have

$$K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}}$$

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:

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

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

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

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  $K_c$ :

$$K_p = \frac{([D]RT)^d([E]RT)^e}{([A]RT)^a([B]RT)^b} = \left( \frac{[D]^d[E]^e}{[A]^a[B]^b} \right) \frac{(RT)^{d+e}}{(RT)^{a+b}} \quad [15.14]$$

Notice that the term in brackets is equal to  $K_c$ , so we can simplify the expression:

$$K_p = K_c(RT)^{(d+e)-(a+b)} = K_c(RT)^{\Delta n} \quad [15.15]$$

The quantity  $\Delta n$  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:

$$\Delta n = (\text{moles of gaseous product}) - (\text{moles of gaseous reactant}) \quad [15.16]$$

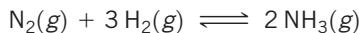
For example, in the  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g)$  reaction, there are 2 mol of product  $\text{NO}_2$  and 1 mol of reactant  $\text{N}_2\text{O}_4$ . Therefore,  $\Delta n = 2 - 1 = 1$ , and  $K_p = K_c(RT)$ , for this reaction. In our derivation gas pressures are expressed as kilopascals and concentrations in moles per liter, thus the appropriate form of the gas constant is  $R = 8.314 \text{ L kPa/mol K}$ . Note that  $K_p$  has the partial pressures expressed in bar. A standard atmosphere is now defined as 1 bar or 100 kPa which is taken into account in the conversion.



## Sample Exercise 15.2

### Converting between $K_c$ and $K_p$

For the Haber process,



$K_c = 9.60$  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 15.15. To apply that equation, we must determine  $\Delta n$  by comparing the number of moles of product with the number of moles of reactants (Equation 15.16).

**Solve** With 2 mol of gaseous products ( $2 \text{NH}_3$ ) and 4 mol of gaseous reactants ( $1 \text{N}_2 + 3 \text{H}_2$ ),  $\Delta n = 2 - 4 = -2$ . (Remember that  $\Delta$  functions are always based on *products minus reactants*.) The temperature is  $273 + 300 = 573$  K. The value for the ideal-gas constant,  $R$ , is  $8.314 \text{ L kPa/mol K}$ . Remember we need to convert to a standard atmosphere which is 100 kPa. Using  $K_c = 9.60$ , we therefore have

$$K_p = K_c (RT)^{\Delta n} = (9.60)(8.314 \times 573)^{-2} \\ = \frac{(9.60)}{(8.314 \times 573)^2} = 4.23 \times 10^{-10}$$

#### ► Practice Exercise

For which of the following reactions is the ratio  $K_p/K_c$  largest at 300 K?

- (a)  $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g)$
- (b)  $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$
- (c)  $\text{Ni}(\text{CO})_4(g) \rightleftharpoons \text{Ni}(s) + 4 \text{CO}(g)$
- (d)  $\text{C}(s) + 2 \text{H}_2(g) \rightleftharpoons \text{CH}_4(g)$

## 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 (100 kPa). For example, if the concentration of a substance in an equilibrium mixture is 0.010 M, its activity is  $0.010 \text{ M}/1 \text{ M} = 0.010$ . 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 assume those differences are small enough that we can neglect them. 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.

## Self-Assessment Exercises

**15.3** What is the equilibrium expression for the reaction:  
 $2 \text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$ ?

- (a)  $K = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]}$
- (b)  $K = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$
- (c)  $K = [\text{HI}]^2$

**15.4** For the equilibrium  $2 \text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$   $K_c = 0.022$  at 490 °C. What is the value of  $K_p$ ?

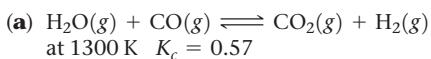
- (a)  $K_p = 0.022$
- (b)  $K_p = 0.14$
- (c)  $K_p = 46$

## Exercises

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

- (a)  $O_2(g) \rightleftharpoons 2O(g)$
- (b)  $Si(s) + 2Cl_2(g) \rightleftharpoons SiCl_4(g)$
- (c)  $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
- (d)  $O_2(g) + 2CO(g) \rightleftharpoons 2CO_2(g)$
- (e)  $HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$
- (f)  $Fe^{2+}(aq) + Ce^{4+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ce^{3+}(aq)$
- (g)  $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

**15.6** Which of the following reactions lies to the right, favoring the formation of products, and which lies to the left, favoring formation of reactants?



**15.7** Which of the following statements are true and which are false? (a) For the reaction  $2A(g) + B(g) \rightleftharpoons A_2B(g)$   $K_c$  and  $K_p$  are numerically the same. (b) It is possible to distinguish  $K_c$  from  $K_p$  by comparing the units used to express the equilibrium constant. (c) For the equilibrium in (a), the value of  $K_c$  increases with increasing pressure.

**15.8** Calculate  $K_c$  at 900 K for  $2CO(g) \rightleftharpoons CO_2(g) + C(s)$  if  $K_p = 0.0572$  at this temperature.

15.3 (b) 15.4 (b)

Answers to Self-Assessment Exercises

## 15.3 | Understanding and Working with Equilibrium Constants



When we have solved a problem involving some calculation, we have emphasized the importance of taking a moment to appraise the answer we get to see if it 'looks about right'. In this way, we can avoid errors, for example, adding an extra zero to a number in some part of the calculation by mistake. Another important skill you will develop is a feel for quantities. Our experience has taught us that a weather forecast of 40 °C tells us that it is going to be a hot day. With a little practice, we will be able to view the numbers we use in chemistry and get a feel for what they represent. For instance, does a particular  $\Delta H$  value represent a large or small amount of energy? If I hold a golf ball-sized sample of something with a density of 10 g/mL will it feel heavy? How does an equilibrium constant of 1000 relate to the yield of product I may hope to get from the reaction? We start

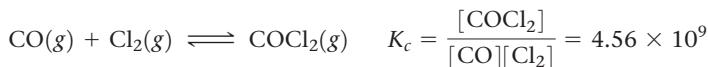
this section by exploring the magnitude of  $K$ . By the end of this section, you should be able to

- Relate the magnitude of an equilibrium constant to the relative amounts of reactants and products present in an equilibrium mixture.
- Manipulate the equilibrium constant to reflect changes in the chemical equation.
- Write the equilibrium expression for a heterogeneous reaction.

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 ( $\text{COCl}_2$ ), a toxic gas used in the manufacture of certain polymers and insecticides:



For the equilibrium constant to be so large, the numerator of the equilibrium expression must be approximately a billion ( $10^9$ ) times larger than the denominator. Thus, the equilibrium concentration of  $\text{COCl}_2$  must be much greater than that of CO or  $\text{Cl}_2$ , 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,

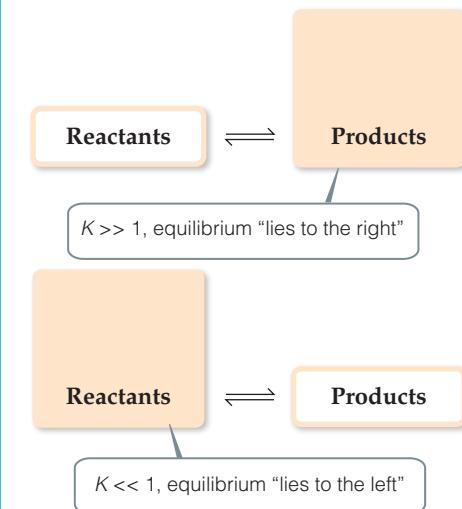
*If  $K \gg 1$  (large  $K$ ): Equilibrium lies to right, products predominate*

*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 reaction rates, not reactant and product concentrations, that are equal at equilibrium.

### Go Figure

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

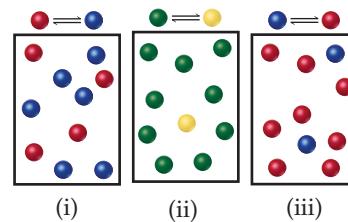


▲ **Figure 15.6** Relationship between magnitude of  $K$  and composition of an equilibrium mixture.

### 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 reactants) to largest (most products).

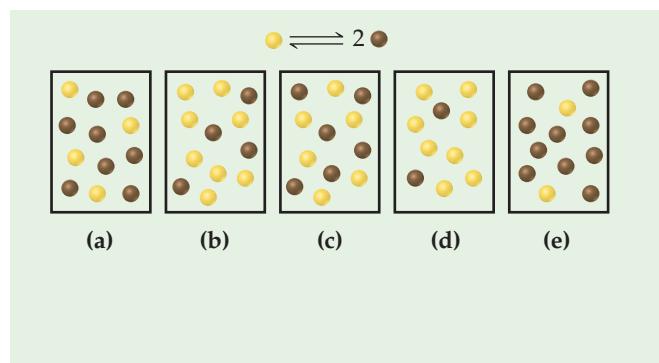
(b) In (i), we have 0.60 mol/L product and 0.40 mol/L reactant, giving  $K_c = 0.60/0.40 = 1.5$ . (You will get the same result by merely dividing the number of spheres of each kind: 6 spheres/4 spheres = 1.5.) In (ii), we have 0.10 mol/L product and 0.90 mol/L reactant, giving  $K_c = 0.10/0.90 = 0.11$  (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).

*Continued*

**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

The equilibrium constant for the reaction  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g)$  at 2 °C is  $K_c = 2.0$ . If each yellow sphere represents 1 mol of  $\text{N}_2\text{O}_4$  and each brown sphere 1 mol of  $\text{NO}_2$ , which of the following 1.0 L containers represents the equilibrium mixture at 2 °C?



## The Direction of the Chemical Equation and K

We have seen that we can represent the  $\text{N}_2\text{O}_4/\text{NO}_2$  equilibrium as

$$\text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g) \quad K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 0.212 \quad (\text{at } 100^\circ\text{C}) \quad [15.17]$$

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



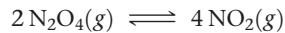
The equilibrium expression is then

$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} = \frac{1}{0.212} = 4.72 \quad (\text{at } 100^\circ\text{C}) \quad [15.18]$$

Equation 15.18 is the reciprocal of the expression in Equation 15.17. *The equilibrium 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  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  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.

## 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,  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g)$  by 2, we have



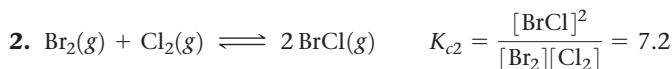
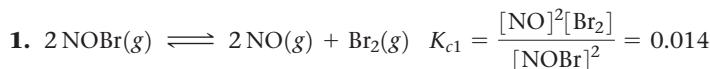
This chemical equation is balanced and might be written this way in some contexts. Therefore, the equilibrium expression for this equation is

$$K_c = \frac{[\text{NO}_2]^4}{[\text{N}_2\text{O}_4]^2}$$

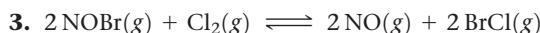
which is the square of the equilibrium expression given in Equation 15.10 for the reaction as written in Equation 15.1:  $[\text{NO}_2]^2/[\text{N}_2\text{O}_4]$ . Because the new equilibrium expression equals the original expression squared, the new equilibrium constant  $K_c$  equals the original constant 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 on how you write the reaction.

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 the manner in which the reaction enthalpy of an unknown reaction can be determined from known reaction enthalpies using Hess's law. For example, consider the following two reactions, their equilibrium expressions, and their equilibrium constants at 100 °C:



The net sum of these two equations is:



You can prove algebraically that the equilibrium expression for the net reaction is the product of the expressions for individual reactions:

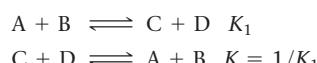
$$K_{c3} = \frac{[\text{NO}]^2[\text{BrCl}]^2}{[\text{NOBr}]^2[\text{Cl}_2]} = \frac{[\text{NO}]^2[\text{Br}_2]}{[\text{NOBr}]^2} \times \frac{[\text{BrCl}]^2}{[\text{Br}_2][\text{Cl}_2]}$$

Thus,

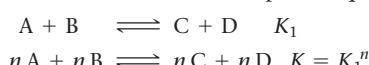
$$K_{c3} = (K_{c1})(K_{c2}) = (0.014)(7.2) = 0.10$$

To summarize:

- 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:



- 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.



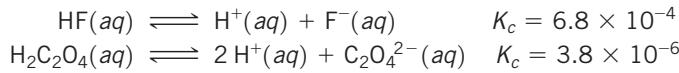
- The equilibrium constant for a net reaction made up by adding *two or more reactions* is the *product* of the equilibrium constants for the individual reactions:



## Sample Exercise 15.4

### Combining Equilibrium Expressions

Given the reactions



determine the value of  $K_c$  for the reaction



### 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 these equations to come up with equations that we can add to give us the desired equation.

**Solve**

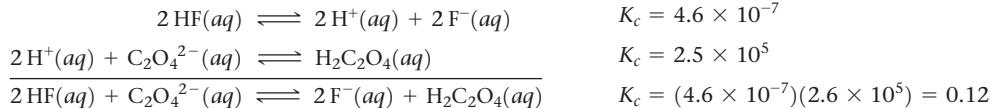
If we multiply the first equation by 2 and make the corresponding change to its equilibrium constant (raising to the power 2), we get



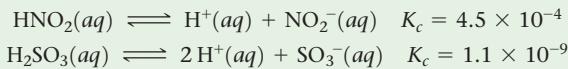
Reversing the second equation and again making the corresponding change to its equilibrium constant (taking the reciprocal) gives



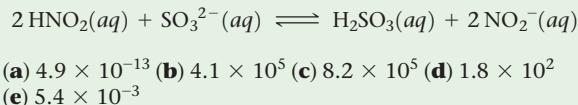
Now, we have two equations that sum to give the net equation, and we can multiply the individual  $K_c$  values to get the desired equilibrium constant.

**► Practice Exercise**

Given the equilibrium constants for the following two reactions in aqueous solution at 25 °C,



what is the value of  $K_c$  for the reaction?



## Heterogeneous Equilibria

Many equilibria involve substances that are all in the same phase. Such equilibria are called **homogeneous equilibria**. The equilibrium between  $\text{N}_2\text{O}_4(g)$  and  $\text{NO}_2(g)$  shown in Figure 15.1 is one such example. In some cases, however, the substances in equilibrium are in different phases, giving rise to **heterogeneous equilibria**. An example occurs when solid lead(II) chloride dissolves in water to form a saturated solution:



This system consists of a solid in equilibrium with two aqueous species. If we want to write the equilibrium expression for this process, we encounter a problem we have not encountered previously: How do we express the concentration of a solid? If we were to carry out experiments starting with varying amounts of products and reactants, we would find that the equilibrium expression for the reaction of Equation 15.19 is

$$K_c = [\text{Pb}^{2+}][\text{Cl}^-]^2 \quad [15.20]$$

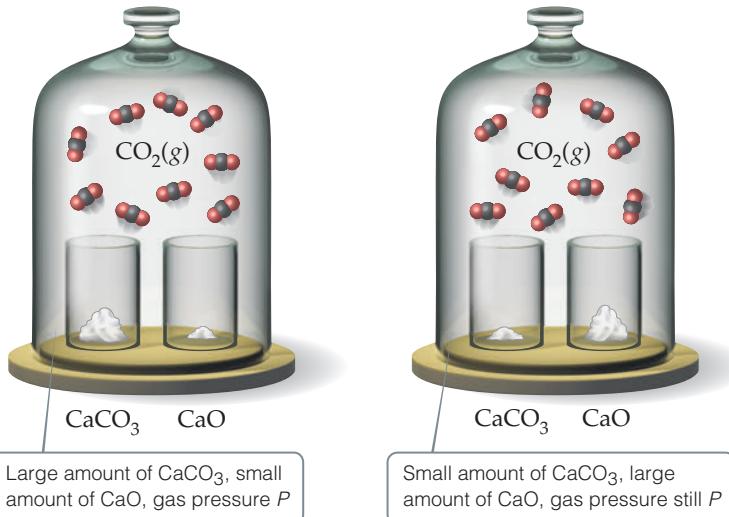
Thus, our problem of how to express the concentration of a solid is not relevant in the end because  $\text{PbCl}_2(s)$  does not show up in the equilibrium expression. More generally, we can state that *whenever a pure solid or a pure liquid is involved in a heterogeneous equilibrium, its concentration is not included in the equilibrium expression*.

The fact that pure solids and pure liquids are excluded from equilibrium 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 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,

 Go Figure

If some of the  $\text{CO}_2(g)$  were released from the bell jar on the left, the seal then restored and the system allowed to return to equilibrium, would the amount of  $\text{CaCO}_3(s)$  increase, decrease, or remain the same?



▲ **Figure 15.7** At a given temperature, the equilibrium pressure of  $\text{CO}_2$  in the bell jars is the same no matter how much of each solid is present.

the reference value is the concentration of the pure substance, so that the activity of any pure solid or liquid is always 1.

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



Omitting the concentrations of the solids from the equilibrium expression gives

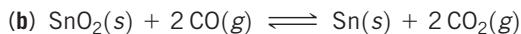
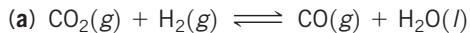
$$K_c = [\text{CO}_2] \quad \text{and} \quad K_p = P_{\text{CO}_2}$$

These equations tell us that at a given temperature, an equilibrium among  $\text{CaCO}_3$ ,  $\text{CaO}$ , and  $\text{CO}_2$  always leads to the same  $\text{CO}_2$  partial pressure as long as all three components are present. As shown in **Figure 15.7**, we have the same  $\text{CO}_2$  pressure regardless of the relative amounts of  $\text{CaO}$  and  $\text{CaCO}_3$ .

 Sample Exercise 15.5

## Writing Equilibrium Expressions for Heterogeneous Reactions

Write the equilibrium expression  $K_c$  for


**SOLUTION**

**Analyze** We are given two chemical equations, both for heterogeneous equilibria, and asked to write the corresponding equilibrium 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 expression is

$$K_c = \frac{[\text{CO}]}{[\text{CO}_2][\text{H}_2]}$$

Because  $\text{H}_2\text{O}$  appears in the reaction as a liquid, its concentration does not appear in the equilibrium expression.

*Continued*

(b) The equilibrium expression is

$$K_c = \frac{[\text{CO}_2]^2}{[\text{CO}]^2}$$

Because  $\text{SnO}_2$  and Sn are pure solids, their concentrations do not appear in the equilibrium expression.

### ► Practice Exercise

Consider the equilibrium that is established in a saturated solution of silver chloride,  $\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightleftharpoons \text{AgCl}(s)$ . If solid  $\text{AgCl}$  is added to this solution, what will happen to the concentration of  $\text{Ag}^+$  and  $\text{Cl}^-$  ions in solution?

- (a)  $[\text{Ag}^+]$  and  $[\text{Cl}^-]$  will both increase (b)  $[\text{Ag}^+]$  and  $[\text{Cl}^-]$  will both decrease (c)  $[\text{Ag}^+]$  will increase and  $[\text{Cl}^-]$  will decrease (d)  $[\text{Ag}^+]$  will decrease and  $[\text{Cl}^-]$  will increase (e) neither  $[\text{Ag}^+]$  nor  $[\text{Cl}^-]$  will change

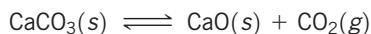
## Sample Exercise 15.6

### Analyzing a Heterogeneous Equilibrium

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

- (a)  $\text{CaCO}_3(s)$
- (b)  $\text{CaO}(s)$  and  $\text{CO}_2(g)$  at a pressure greater than the value of  $K_p$
- (c)  $\text{CaCO}_3(s)$  and  $\text{CO}_2(g)$  at a pressure greater than the value of  $K_p$
- (d)  $\text{CaCO}_3(s)$  and  $\text{CaO}(s)$

Determine whether or not each mixture can attain the equilibrium



### 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, some calcium carbonate must be present. For the reverse process to occur, both calcium oxide and carbon dioxide must be present. 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)  $\text{CaCO}_3$  simply decomposes, forming  $\text{CaO}(s)$  and  $\text{CO}_2(g)$  until the equilibrium pressure of  $\text{CO}_2$  is attained. There must be enough  $\text{CaCO}_3$ , however, to allow the  $\text{CO}_2$  pressure to reach equilibrium. (b)  $\text{CO}_2$  continues to combine with  $\text{CaO}$  until the partial pressure of the  $\text{CO}_2$  decreases to the equilibrium value. (c) Because there is no  $\text{CaO}$  present,

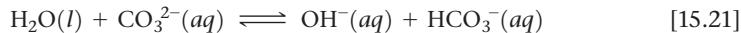
equilibrium cannot be attained; there is no way the  $\text{CO}_2$  pressure can decrease to its equilibrium value (which would require some  $\text{CO}_2$  to react with  $\text{CaO}$ ). (d) The situation is essentially the same as in (a):  $\text{CaCO}_3$  decomposes until equilibrium is attained. The presence of  $\text{CaO}$  initially makes no difference.

### ► Practice Exercise

If 8.0 g of  $\text{NH}_4\text{HS}(s)$  is placed in a sealed vessel with a volume of 1.0 L and heated to 200 °C the reaction  $\text{NH}_4\text{HS}(s) \rightleftharpoons \text{NH}_3(g) + \text{H}_2\text{S}(g)$  will occur. When the system comes to equilibrium, some  $\text{NH}_4\text{HS}(s)$  is still present. Which of the following changes will lead to a reduction in the amount of  $\text{NH}_4\text{HS}(s)$  that is present, assuming in all cases that equilibrium is re-established following the change?

- (a) Adding more  $\text{NH}_3(g)$  to the vessel (b) Adding more  $\text{H}_2\text{S}(g)$  to the vessel (c) Adding more  $\text{NH}_4\text{HS}(s)$  to the vessel (d) Increasing the volume of the vessel (e) Decreasing the volume of the vessel

When a solvent is a reactant or product in an equilibrium, its concentration is omitted from the equilibrium 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,



gives an equilibrium expression that does not contain  $[\text{H}_2\text{O}]$ :

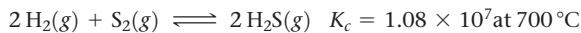
$$K_c = \frac{[\text{OH}^-][\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} \quad [15.22]$$

## Self-Assessment Exercises

- 15.9** For the reaction  $\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{SO}_3(g)$   $K_c = 855$  at 1000 K. Do the reactants or the product dominate the equilibrium mixture?
- The reactants
  - The product
- 15.10** For the reaction  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ , the equilibrium constant  $K_c = 0.0059$  at 300 K. What is the equilibrium constant for the reverse reaction  $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$ , at 300 K?
- $K_c = 0.0059$
  - $K_c = -0.0059$
  - $K_c = 169$

## Exercises

- 15.12** Consider the following equilibrium:



- (a) Calculate  $K_p$ . (b) Does the equilibrium mixture contain mostly  $\text{H}_2$  and  $\text{S}_2$  or mostly  $\text{H}_2\text{S}$ ? (c) Calculate the value of  $K_c$  if you rewrote the equation  $\text{H}_2(g) + \frac{1}{2}\text{S}_2(g) \rightleftharpoons \text{H}_2\text{S}(g)$ .

- 15.13** Consider the following equilibrium, for which  $K_p = 7.62$  at  $480^\circ\text{C}$ :



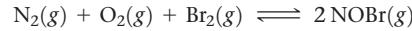
- (a) What is the value of  $K_p$  for the reaction  $4\text{HCl}(g) + \text{O}_2(g) \rightleftharpoons 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(g)$ ?  
(b) What is the value of  $K_p$  for the reaction  $\text{Cl}_2(g) + \text{H}_2\text{O}(g) \rightleftharpoons 2\text{HCl}(g) + \frac{1}{2}\text{O}_2(g)$ ?

- 15.11** Write the equilibrium constant expression for the reaction  $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$

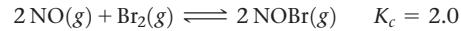
(a)  $K = [\text{Ag}^+][\text{Cl}^-]$

(b)  $K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$

- 15.14** Consider the equilibrium



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



- 15.15** Consider the equilibrium  $\text{Na}_2\text{O}(s) + \text{SO}_2(g) \rightleftharpoons \text{Na}_2\text{SO}_3(s)$ . (a) Write the equilibrium expression for this reaction in terms of partial pressures. (b) All the compounds in this reaction are soluble in water. Rewrite the equilibrium expression in terms of molarities for the aqueous reaction.

15.9 (b)    15.10 (c)    15.11 (a)

 Answers to Self-Assessment Exercises

## 15.4 | Calculating Equilibrium Constants



In this section, we are performing calculations using equilibrium expressions and the associated constants. In some cases, they may seem complicated but having a clear working method allows us to follow a logical procedure to get to the desired answer. By the end of this section, you should be able to

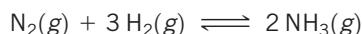
- Perform calculations of different sorts involving equilibrium expressions

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 expression for the reaction.

## Sample Exercise 15.7

### 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 bar H<sub>2</sub>, 2.46 bar N<sub>2</sub>, and 0.166 bar NH<sub>3</sub>. From these data, calculate the equilibrium constant  $K_p$  for the reaction



#### 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

$$K_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{0.166^2}{(249.3)(747.8)^3} = 2.71 \times 10^{-9}$$

#### ► Practice Exercise

An aqueous solution of acetic acid is found to have the following equilibrium concentrations at 25 °C: [CH<sub>3</sub>COOH] = 1.65 × 10<sup>-2</sup> M; [H<sup>+</sup>] = 5.44 × 10<sup>-4</sup> M; and [CH<sub>3</sub>COO<sup>-</sup>] = 5.44 × 10<sup>-4</sup> M. Calculate the equilibrium constant  $K_c$  for the ionization of acetic acid at 25 °C. The reaction is



Often, we do not know the equilibrium concentrations of all species in an equilibrium mixture. If we know the initial concentrations and 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:

#### How to Determine Concentrations of Unknown Species in an Equilibrium Mixture

1. Tabulate all known initial and equilibrium concentrations of the species that appear in the equilibrium 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 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.

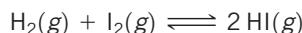
The best way to illustrate this procedure is by example, as we do in Sample Exercise 15.8.



## Sample Exercise 15.8

### Calculating $K_c$ from Initial and Equilibrium Concentrations

A reaction vessel containing  $1.000 \times 10^{-3} M$   $H_2$  gas and  $2.000 \times 10^{-3} M$   $I_2$  gas is heated to  $448^\circ C$  where the following reaction takes place



What is the value of the equilibrium constant  $K_c$  if once the system comes to equilibrium at  $448^\circ C$  the concentration of  $HI$  is  $1.87 \times 10^{-3} M$ ?

#### 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

- (1) 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.
- (2) We calculate the change in  $HI$  concentration, which is the difference between the equilibrium and initial values:

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

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

- (3) We use the coefficients in the balanced equation to relate the change in  $[HI]$  to the changes in  $[H_2]$  and  $[I_2]$ :

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

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

- (4) 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:

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

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

- (5) Our table now is complete (with equilibrium concentrations in blue for emphasis):

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

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

In Section 15.1, we discussed the equilibrium between  $N_2O_4(g)$  and  $NO_2(g)$ . Let's return to that equation in a quantitative example. When 9.2 g of frozen  $N_2O_4$  is added to a 0.50 L reaction vessel that is heated to 400 K and allowed to come to equilibrium, the concentration of  $N_2O_4$  is determined to be 0.057 M. Given this information, what is the value of  $K_c$  for the reaction  $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$  at 400 K? (a) 0.23 (b) 0.36 (c) 0.13 (d) 1.4 (e) 2.5

## 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.
- If  $K$  is very small (that is, much less than 1), the equilibrium mixture contains mostly 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  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$  (Equation 15.6),  $K_c = 0.105$  at  $472^\circ\text{C}$ . Suppose we place 2.00 mol of  $\text{H}_2$ , 1.00 mol of  $\text{N}_2$ , and 2.00 mol of  $\text{NH}_3$  in a 1.00 L container at  $472^\circ\text{C}$ . How will the mixture react to reach equilibrium? Will  $\text{N}_2$  and  $\text{H}_2$  react to form more  $\text{NH}_3$ , or will  $\text{NH}_3$  decompose to  $\text{N}_2$  and  $\text{H}_2$ ?

To answer this question, we substitute the starting concentrations of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  into the equilibrium expression and compare its value to the equilibrium constant:

$$\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(2.00)^2}{(1.00)(2.00)^3} = 0.500 \quad \text{whereas } K_c = 0.105 \quad [15.23]$$

To reach equilibrium, the quotient  $[\text{NH}_3]^2/[\text{N}_2][\text{H}_2]^3$  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  $[\text{NH}_3]$  decreases and  $[\text{N}_2]$  and  $[\text{H}_2]$  increase. Thus, the reaction proceeds toward equilibrium by forming  $\text{N}_2$  and  $\text{H}_2$  from  $\text{NH}_3$ ; 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 expression.*

Therefore, for the general reaction



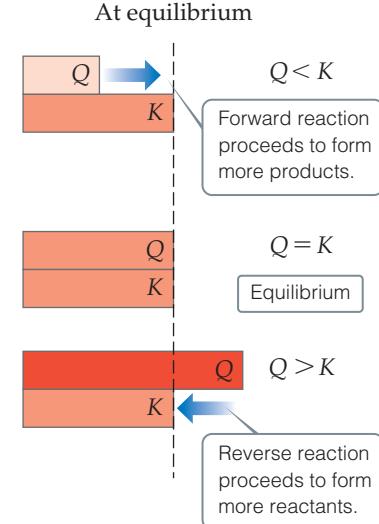
the reaction quotient in terms of molar concentrations is

$$Q_c = \frac{[\text{D}]^d [\text{E}]^e}{[\text{A}]^a [\text{B}]^b} \quad [15.24]$$

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 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 expression of Equation 15.23, 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 15.24 for our reaction. To determine whether 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  $K_p$ . There are three possible scenarios (Figure 15.8), which can be summarized as follows:



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

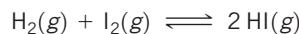
### How to Use $Q$ to Analyze Reaction Progress

- $Q < K$ : 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.
- $Q = K$ : The reaction quotient equals the equilibrium constant only if the system is at equilibrium.
- $Q > K$ : The concentration of products is too large and that of reactants too small. The reaction achieves equilibrium by forming more reactants; it proceeds from right to left.

### Sample Exercise 15.9

#### Predicting the Direction of Approach to Equilibrium

At 448 °C, the equilibrium constant  $K_c$  for the reaction



is 50.5. Predict in which direction the reaction proceeds to reach equilibrium if we start with  $2.0 \times 10^{-2}$  mol of HI,  $1.0 \times 10^{-2}$  mol of H<sub>2</sub>, and  $3.0 \times 10^{-2}$  mol of I<sub>2</sub> 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 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

$$\begin{aligned} [\text{HI}] &= 2.0 \times 10^{-2} \text{ mol}/2.00 \text{ L} = 1.0 \times 10^{-2} \text{ M} \\ [\text{H}_2] &= 1.0 \times 10^{-2} \text{ mol}/2.00 \text{ L} = 5.0 \times 10^{-3} \text{ M} \\ [\text{I}_2] &= 3.0 \times 10^{-2} \text{ mol}/2.00 \text{ L} = 1.5 \times 10^{-2} \text{ M} \end{aligned}$$

The reaction quotient is therefore

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.0 \times 10^{-2})^2}{(5.0 \times 10^{-3})(1.5 \times 10^{-2})} = 1.3$$

Because  $Q_c < K_c$ , the concentration of HI must increase and the concentrations of H<sub>2</sub> and I<sub>2</sub> must decrease to reach equilibrium; the reaction as written proceeds left to right to attain equilibrium.

#### ► Practice Exercise

Which of the following statements accurately describes what would happen to the direction of the reaction described in this sample exercise, if the size of the container were different from 2.00 L? (a) The reaction would proceed in the opposite direction (from right to left) if the container volume were reduced sufficiently. (b) The reaction would proceed in the opposite direction if the container volume were expanded sufficiently. (c) The direction of this reaction does not depend on the volume of the container.

### 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 expression to derive an equation that must be solved for an unknown quantity, as demonstrated in Sample Exercise 15.10.

### Sample Exercise 15.10

#### Calculating Equilibrium Concentrations

For the Haber process,  $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$ ,  $K_p = 1.41 \times 10^{-9}$ , at 500 °C. In an equilibrium mixture of the three gases at 500 °C, the partial pressure of H<sub>2</sub> is 94.03 bar and that of N<sub>2</sub> is 43.77 bar. What is the partial pressure of NH<sub>3</sub> in this equilibrium mixture?

*Continued*

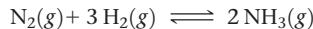
**SOLUTION**

**Analyze** We are given an equilibrium constant,  $K_p$ , and the equilibrium partial pressures of two of the three substances in the equation ( $\text{N}_2$  and  $\text{H}_2$ ), and we are asked to calculate the equilibrium partial pressure for the third substance ( $\text{NH}_3$ ).

**Plan** We can set  $K_p$  equal to the equilibrium 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:



Equilibrium pressure bar    43.77 bar    94.03 bar     $x$

Because we do not know the equilibrium pressure of  $\text{NH}_3$ , we represent it with  $x$ . At equilibrium, the pressures must satisfy the equilibrium expression:

$$K_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{x^2}{(43.77)(94.03)^3} = 1.41 \times 10^{-9}$$

We now rearrange the equation to solve for  $x$ :

$$x^2 = (1.41 \times 10^{-9})(43.77)(94.03)^3 = 5.14 \times 10^{-2}$$

$$x = \sqrt{5.14 \times 10^{-2}} = 0.227 \text{ bar} = P_{\text{NH}_3}$$

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

$$K_p = \frac{(0.227)^2}{(43.77)(94.03)^3} = 1.41 \times 10^{-9}$$

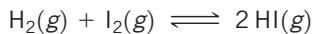
**► Practice Exercise**

At 500 K, the reaction  $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$  has  $K_p = 50.4$ . In an equilibrium mixture at 500 K, the partial pressure of  $\text{PCl}_5$  is 87.14 kPa and that of  $\text{PCl}_3$  is 34.46 kPa. What is the partial pressure of  $\text{Cl}_2$  in the equilibrium mixture?

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 15.11. The calculations frequently involve the quadratic formula, as you will see in this exercise.

**Sample Exercise 15.11****Calculating Equilibrium Concentrations from Initial Concentrations**

A 1.000 L flask is filled with 1.000 mol of  $\text{H}_2(g)$  and 2.000 mol of  $\text{I}_2(g)$  at 448 °C. The value of the equilibrium constant  $K_c$  for the reaction



at 448 °C is 50.5. What are the equilibrium concentrations of  $\text{H}_2$ ,  $\text{I}_2$ , and  $\text{HI}$  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 15.8, where we calculated an equilibrium constant using initial concentrations.

**Solve**

- (1) We note the initial concentrations of

$\text{H}_2$  and  $\text{I}_2$ :

$$[\text{H}_2] = 1.000 \text{ M} \quad \text{and} \quad [\text{I}_2] = 2.000 \text{ M}$$

- (2) We construct a table in which we tabulate the initial concentrations:

	$\text{H}_2(g)$	$+$	$\text{I}_2(g)$	$\rightleftharpoons$	$2 \text{HI}(g)$
Initial concentration (M)	1.000		2.000		0
Change in concentration (M)					
Equilibrium concentration (M)					

- (3) We use the stoichiometry of the reaction to determine the changes in concentration that occur as the reaction proceeds to equilibrium. The H<sub>2</sub> and I<sub>2</sub> concentrations will decrease as equilibrium is established and that of HI will increase. Let's represent the change in concentration of H<sub>2</sub> by  $x$ . The balanced chemical equation tells us that for each  $x$  mol of H<sub>2</sub> that reacts,  $x$  mol of I<sub>2</sub> are consumed and  $2x$  mol of HI are produced:

$\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g)$			
Initial concentration (M)	1.000	2.000	0
Change in concentration (M)	$-x$	$-x$	$+2x$
Equilibrium concentration (M)			

- (4) 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:

$\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g)$			
Initial concentration (M)	1.000	2.000	0
Change in concentration (M)	$-x$	$-x$	$+2x$
Equilibrium concentration (M)	$1.000 - x$	$2.000 - x$	$2x$

- (5) We substitute the equilibrium concentrations into the equilibrium expression and solve for  $x$ :

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)} = 50.5$$

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  $x$ :

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

When we substitute  $x = 2.323$  into the expressions for the equilibrium concentrations, we find *negative* concentrations of H<sub>2</sub> and I<sub>2</sub>. Because a negative concentration is not chemically meaningful, we reject this solution. We then use  $x = 0.935$  to find the equilibrium concentrations:

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

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

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

$$[\text{H}_2] = 1.000 - x = 0.065 \text{ M}$$

$$[\text{I}_2] = 2.000 - x = 1.065 \text{ M}$$

$$[\text{HI}] = 2x = 1.87 \text{ M}$$

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

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(1.87)^2}{(0.065)(1.065)} = 51$$

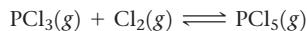
**Comment** Whenever you use a quadratic equation to solve an equilibrium problem, one of the solutions to the equation will give you a value that leads to negative concentrations and thus is not chemically meaningful. Reject this solution to the quadratic equation.

### ► Practice Exercise

For the equilibrium  $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$ , the equilibrium constant  $K_p$  is 50.4 at 500 K. A gas cylinder at 500 K is charged with  $\text{PCl}_5(g)$  at an initial pressure of 168.2 kPa. What are the equilibrium pressures of  $\text{PCl}_5$ ,  $\text{PCl}_3$ , and  $\text{Cl}_2$  at this temperature?

## Self-Assessment Exercise

- 15.16** In an experiment, 0.200 mol of  $\text{PCl}_3(g)$  and 0.100 mol of  $\text{Cl}_2(g)$  were mixed in a 1.00 L container at 250 °C. When equilibrium was established, it was found that  $[\text{PCl}_5] = 0.091$ . Calculate the value of  $K_c$  at this temperature.



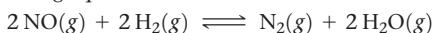
(a)  $K = 0.22$

(b)  $K = 93$

## Exercises

**15.17** Methanol ( $\text{CH}_3\text{OH}$ ) is produced commercially by the catalyzed reaction of carbon monoxide and hydrogen:  $\text{CO}(g) + 2\text{H}_2(g) \rightleftharpoons \text{CH}_3\text{OH}(g)$ . An equilibrium mixture in a 10.00 L vessel is found to contain 0.050 mol  $\text{CH}_3\text{OH}$ , 0.850 mol CO, and 0.750 mol  $\text{H}_2$  at 500 K. Calculate  $K_c$  at this temperature.

**15.18** A mixture of 0.140 mol of NO, 0.060 mol of  $\text{H}_2$ , and 0.260 mol of  $\text{H}_2\text{O}$  is placed in a 2.0 L vessel at 330 K. Assume that the following equilibrium is established:

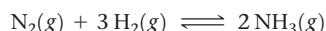


At equilibrium  $[\text{H}_2] = 0.010\text{ M}$ . **(a)** Calculate the equilibrium concentrations of NO,  $\text{N}_2$ , and  $\text{H}_2\text{O}$ . **(b)** Calculate  $K_c$ .

**15.19** 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  $1.50 \times 10^{-6}\text{ M}$ . Drug A is introduced into the protein solution at an initial concentration of  $2.00 \times 10^{-6}\text{ M}$ . Drug B is introduced into a separate, identical protein solution at an initial concentration of  $2.00 \times 10^{-6}\text{ M}$ . At equilibrium, the drug A–protein solution has an A–protein complex concentration of  $1.00 \times 10^{-6}\text{ M}$ , and the drug B solution has a B–protein complex concentration of  $1.40 \times 10^{-6}\text{ M}$ . 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?

**15.20** **(a)** If  $Q_c > K_c$ , how must the reaction proceed to reach equilibrium? **(b)** 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?

**15.21** As shown in Table 15.2,  $K_p$  for the equilibrium



is  $4.39 \times 10^{-9}$  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.

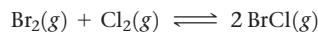
**(a)** 9.93 MPa  $\text{NH}_3$ , 4.56 MPa  $\text{N}_2$ , 5.57 MPa  $\text{H}_2$

**(b)** 5.78 MPa  $\text{NH}_3$ , 14.49 MPa  $\text{N}_2$ , no  $\text{H}_2$

**(c)** 1.32 MPa  $\text{NH}_3$ , 2.74 MPa  $\text{N}_2$ , 8.31 MPa  $\text{H}_2$

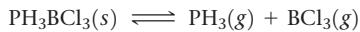
**15.22** For  $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$ ,  $K_p = 3.0 \times 10^2$  at 700 K. In a 2.00 L vessel, the equilibrium mixture contains 1.17 g of  $\text{SO}_3$  and 0.105 g of  $\text{O}_2$ . How many grams of  $\text{SO}_2$  are in the vessel?

**15.23** For the equilibrium



at 400 K,  $K_c = 7.0$ . If 0.25 mol of  $\text{Br}_2$  and 0.55 mol of  $\text{Cl}_2$  are introduced into a 3.0 L container at 400 K, what will be the equilibrium concentrations of  $\text{Br}_2$ ,  $\text{Cl}_2$ , and  $\text{BrCl}$ ?

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



**(a)** Calculate the equilibrium concentrations of  $\text{PH}_3$  and  $\text{BCl}_3$  if a solid sample of  $\text{PH}_3\text{BCl}_3$  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  $\text{PH}_3\text{BCl}_3(s)$  that must be added to the flask to achieve equilibrium?

15.16 (b)

Answers to Self-Assessment Exercises



## 15.5 | 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<sub>2</sub> and H<sub>2</sub>, 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<sub>3</sub> formed under a variety of conditions. By the end of this section, you should be able to

- Use Le Châtelier's principle to predict how changing the concentrations, volume, or temperature of a system at equilibrium affects the equilibrium position.

Some of Haber's results are shown in **Figure 15.9**. Notice that the percent of NH<sub>3</sub> 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.*

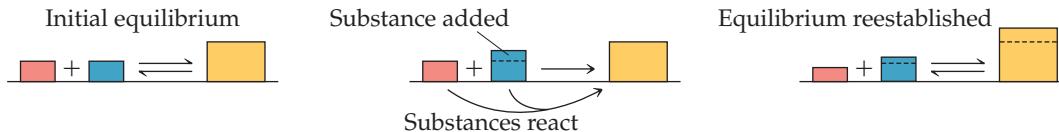
### Le Châtelier's Principle



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 counteract the effect of the disturbance.

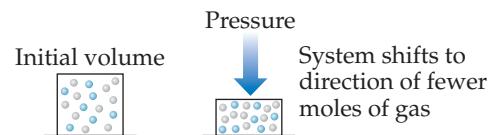
#### Concentration: adding or removing a reactant or product

*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 the 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.*



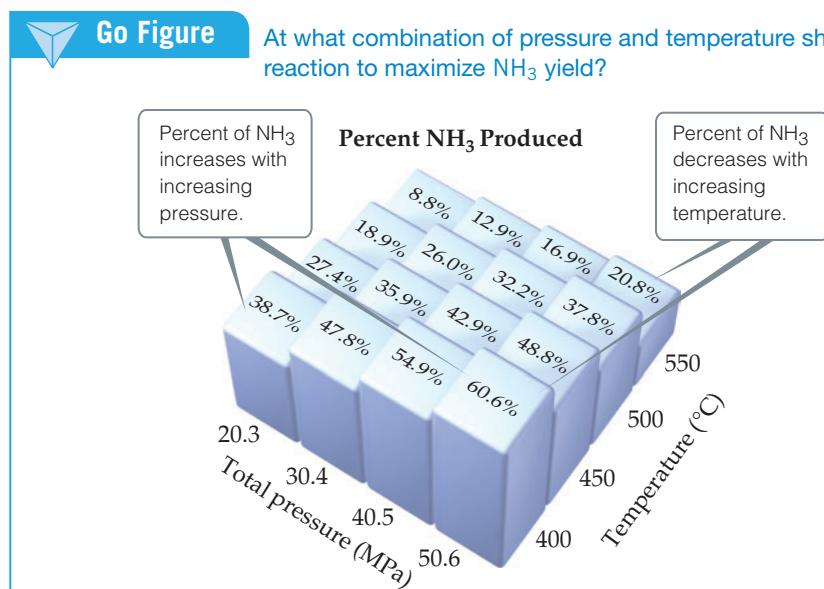
#### Temperature:

*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 reagent," namely, heat.*



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.

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



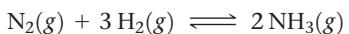
▲ Figure 15.9 Effect of temperature and pressure on  $\text{NH}_3$  yield in the Haber process. Each mixture was produced by starting with a 3:1 molar mixture of  $\text{H}_2$  and  $\text{N}_2$ .

### 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.

*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  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$ :

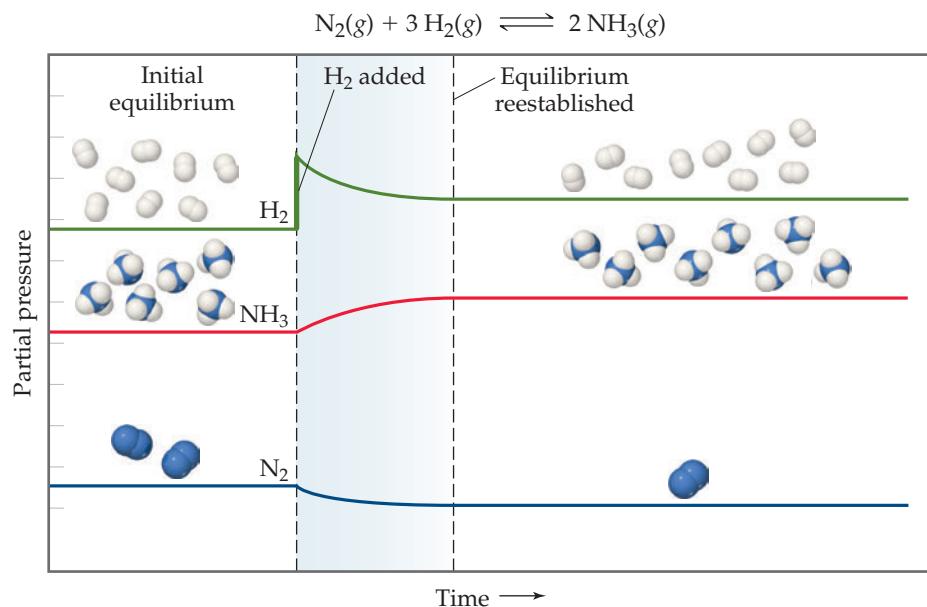


Adding  $\text{H}_2$  causes the system to shift so as to reduce the increased concentration of  $\text{H}_2$  (Figure 15.10). This change can occur only if the reaction consumes  $\text{H}_2$  and simultaneously consumes  $\text{N}_2$  to form more  $\text{NH}_3$ . Adding  $\text{N}_2$  to the equilibrium mixture likewise causes the reaction to shift toward forming more  $\text{NH}_3$ . Removing  $\text{NH}_3$  also causes a shift toward producing more  $\text{NH}_3$ , whereas adding  $\text{NH}_3$  to the system at equilibrium causes the reaction to shift in the direction that reduces the increased  $\text{NH}_3$  concentration: Some of the added ammonia decomposes to form  $\text{N}_2$  and  $\text{H}_2$ . All of these “shifts” are entirely consistent with predictions that we would make by comparing the reaction quotient  $Q$  with the equilibrium constant  $K$ .

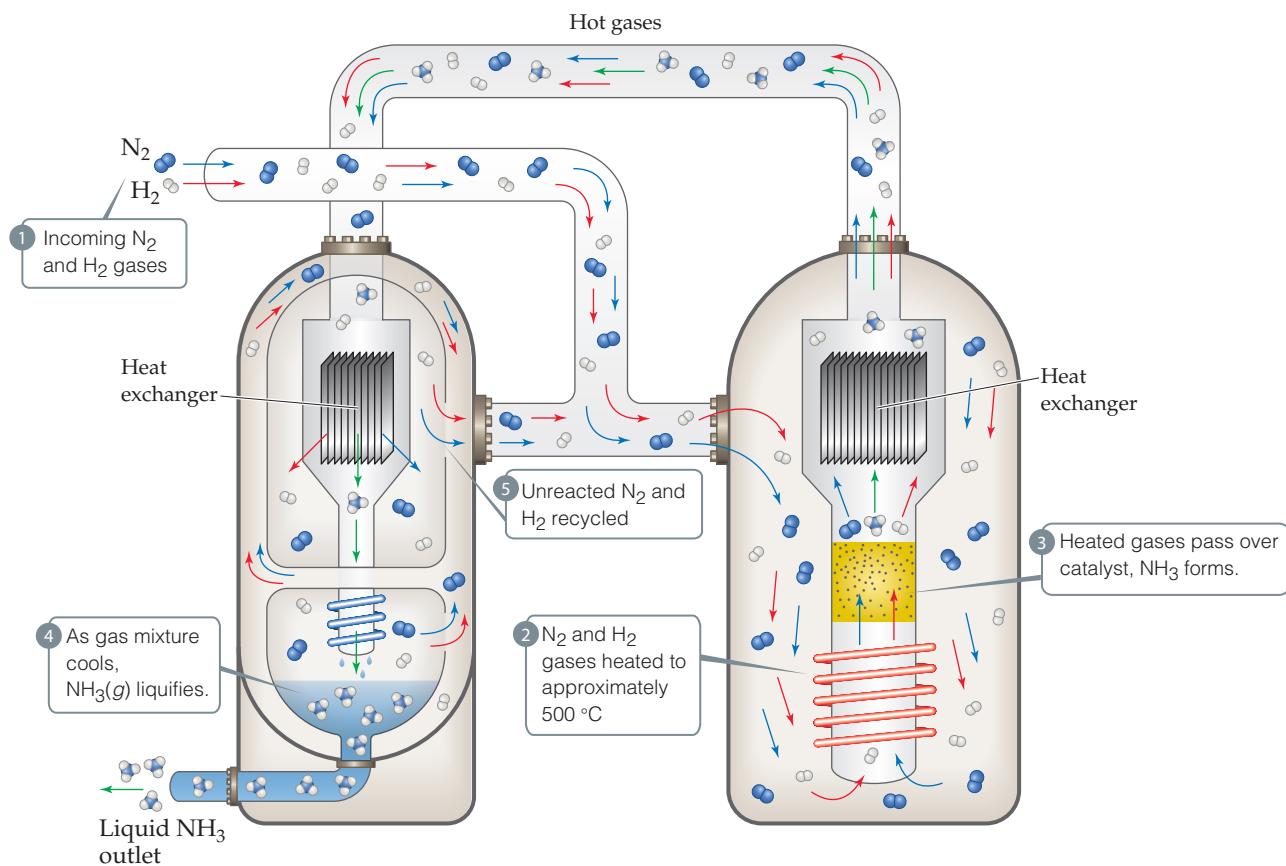
In the Haber reaction, therefore, removing  $\text{NH}_3$  from an equilibrium mixture of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  causes the reaction to shift right to form more  $\text{NH}_3$ . If the  $\text{NH}_3$  can be removed continuously as it is produced, the yield can be increased dramatically. In the industrial production of ammonia, the  $\text{NH}_3$  is continuously removed by selectively liquefying it (Figure 15.11). (The boiling point of  $\text{NH}_3$ ,  $-33^\circ\text{C}$ , is much higher than those of  $\text{N}_2$ ,  $-196^\circ\text{C}$ , and  $\text{H}_2$ ,  $-253^\circ\text{C}$ .) The liquid  $\text{NH}_3$  is removed, and the  $\text{N}_2$  and  $\text{H}_2$  are recycled to form more  $\text{NH}_3$ . As a result of the product being continuously removed, the reaction is driven essentially to completion.

**Go Figure**

Why does the nitrogen concentration decrease after hydrogen is added?



**▲ Figure 15.10** Effect of adding  $\text{H}_2$  to an equilibrium mixture of  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$ . Adding  $\text{H}_2$  causes the reaction as written to shift to the right, consuming some  $\text{N}_2$  to produce more  $\text{NH}_3$ .



**▲ Figure 15.11** Diagram of the industrial production of ammonia. Incoming  $\text{N}_2(g)$  and  $\text{H}_2(g)$  are heated to approximately  $500^\circ\text{C}$  and passed over a catalyst. When the resultant  $\text{N}_2$ ,  $\text{H}_2$ , and  $\text{NH}_3$  mixture is cooled, the  $\text{NH}_3$  liquefies and is removed from the mixture, shifting the reaction to produce more  $\text{NH}_3$ .

## 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).

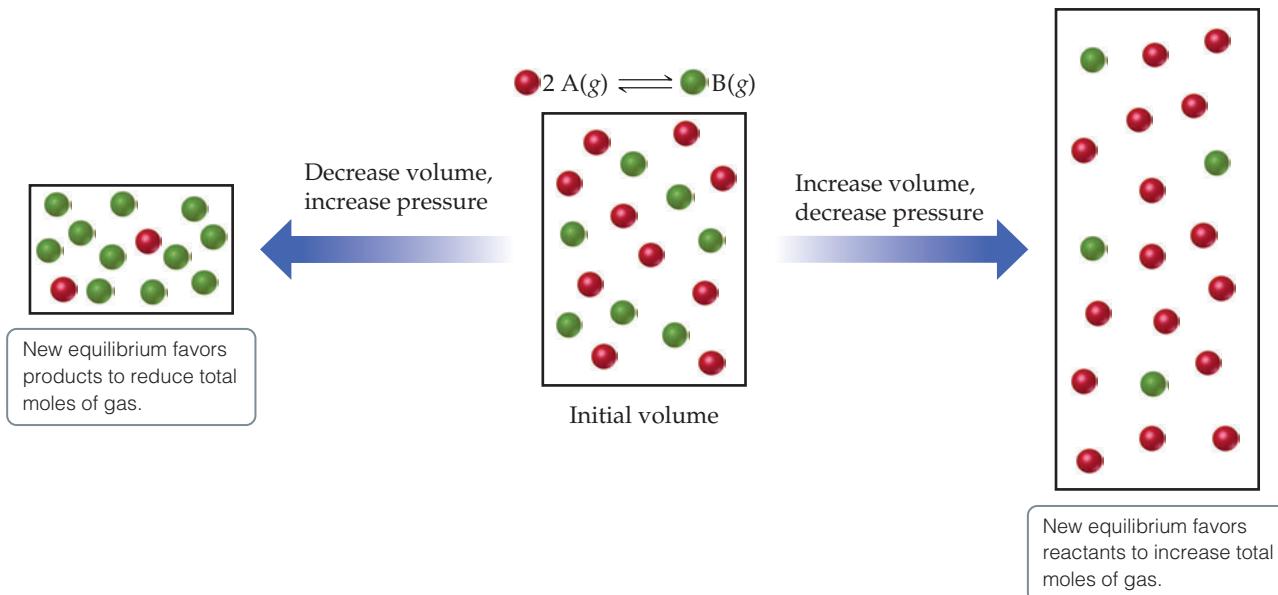
In the reaction  $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$ , four molecules of reactant are consumed for every two molecules of product produced. Consequently, an increase in pressure (caused by a decrease in volume) shifts the reaction in the direction that produces fewer gas molecules, which leads to the formation of more  $\text{NH}_3$ , as indicated in Figure 15.9. In the reaction  $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g)$ , 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 15.7, we calculated  $K_p = 2.71 \times 10^{-9}$  for the Haber reaction,  $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$ , in an equilibrium mixture at  $472^\circ\text{C}$  containing 249.3 kPa  $\text{H}_2$ , 747.8 kPa  $\text{N}_2$ , and 16.82 kPa  $\text{NH}_3$ . 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  $P_{\text{H}_2} = 1495.6$  kPa,  $P_{\text{N}_2} = 498.6$  kPa, and  $P_{\text{NH}_3} = 33.64$  kPa. The reaction quotient would then no longer equal the equilibrium constant:

$$Q_p = \frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = \frac{(33.6 \text{ kPa})^2}{(498.6 \text{ kPa})(1495.6 \text{ kPa})^3} = 6.79 \times 10^{-10} \neq K_p$$

Because  $Q_p < K_p$ , the system would no longer be at equilibrium. Equilibrium would be reestablished by increasing  $P_{\text{NH}_3}$  and decreasing both  $P_{\text{N}_2}$  and  $P_{\text{H}_2}$  until  $Q_p = K_p = 2.71 \times 10^{-9}$ . 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

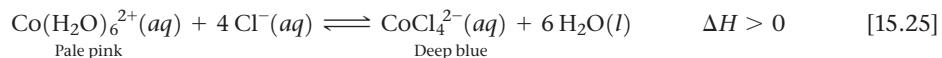


▲ Figure 15.12 Pressure and Le Châtelier's principle.

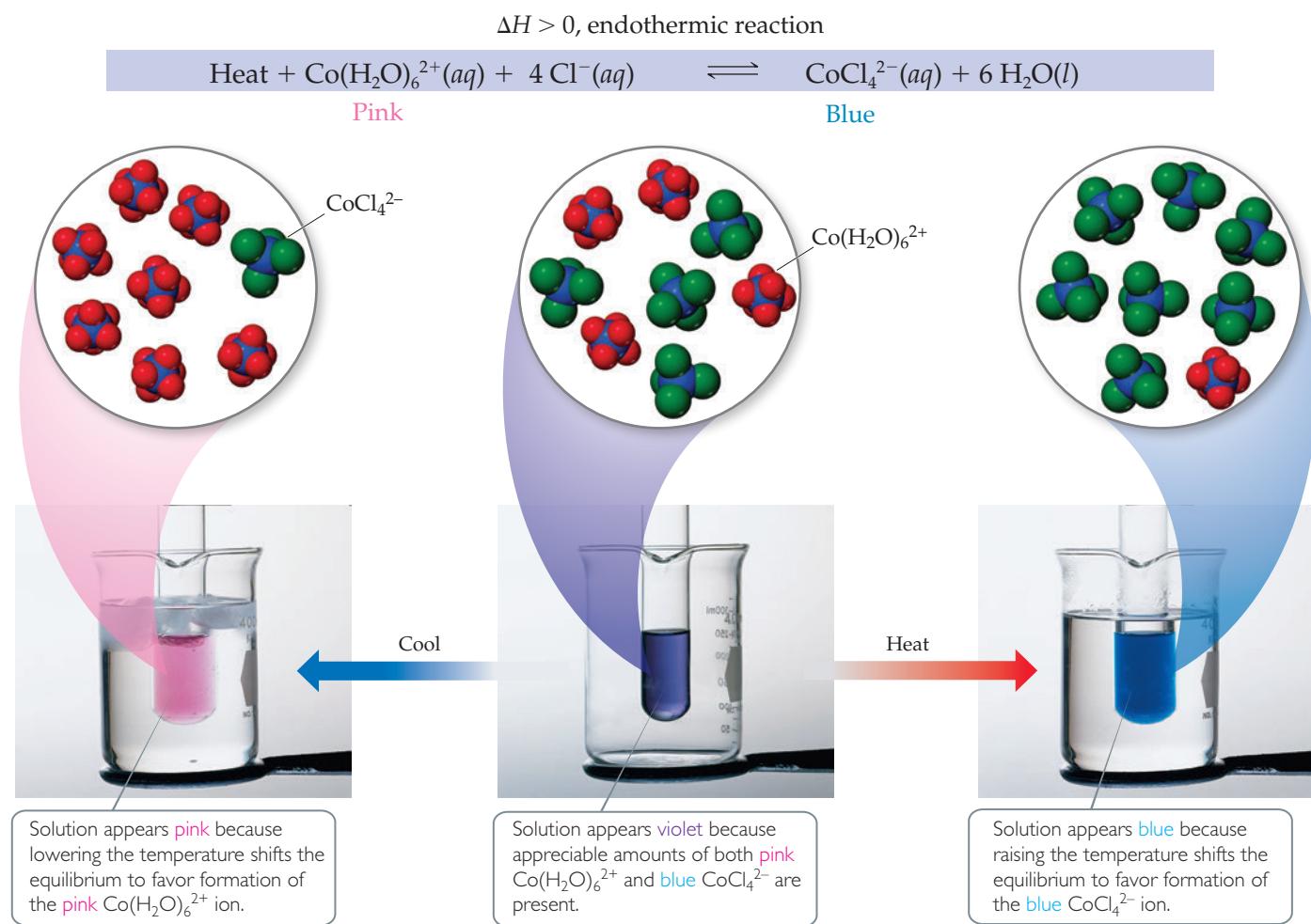
with a change in concentration of a reactant or product. However, the *total* pressure in the reaction vessel might also be increased by adding a gas that is not involved in the equilibrium. For example, argon might be added to the ammonia equilibrium system. The argon would not alter the *partial* pressures 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 ( $\text{CoCl}_2$ ) is dissolved in hydrochloric acid,  $\text{HCl}(aq)$ , in the endothermic reaction



Because  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  is pink and  $\text{CoCl}_4^{2-}$  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  $\text{CoCl}_4^{2-}$ . Cooling the solution leads to a pink solution, indicating that the equilibrium has shifted to produce more  $\text{Co}(\text{H}_2\text{O})_6^{2+}$ . We can monitor this reaction by spectroscopic methods, measuring the concentration of all species at the different temperatures. We can then calculate the equilibrium constant at each temperature. How do we explain why the equilibrium constants and therefore the position of equilibrium both depend on temperature?



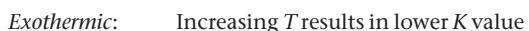
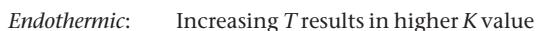
▲ **Figure 15.13** Temperature and Le Châtelier's principle. In the molecular level views, only the  $\text{CoCl}_4^{2-}$  and  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  ions are shown for clarity.

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*:



*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.*

In an endothermic reaction, such as Equation 15.25, 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.

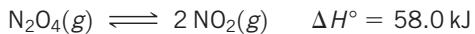


Cooling a reaction has the opposite effect. As we lower the temperature, the equilibrium shifts in the direction that produces heat. Thus, cooling an endothermic reaction shifts the equilibrium to the left, decreasing  $K$ , as shown in Figure 15.13, and cooling an exothermic reaction shifts the equilibrium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

## Sample Exercise 15.12

### Using Le Châtelier's Principle to Predict Shifts in Equilibrium

Consider the equilibrium



In which direction will the equilibrium shift when (a)  $\text{N}_2\text{O}_4$  is added, (b)  $\text{NO}_2$  is removed, (c) the pressure is increased by addition of  $\text{N}_2(g)$ , (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.

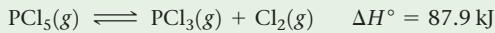
### Solve

- (a) The system will adjust to decrease the concentration of the added  $\text{N}_2\text{O}_4$ , so the equilibrium shifts to the right, in the direction of the product.
- (b) The system will adjust to the removal of  $\text{NO}_2$  by shifting to the side that produces more  $\text{NO}_2$ ; thus, the equilibrium shifts to the right.
- (c) Adding  $\text{N}_2$  will increase the total pressure of the system, but  $\text{N}_2$  is not involved in the reaction. The partial pressures of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  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  $\text{N}_2\text{O}_4$ . Note that only this last change also affects the value of the equilibrium constant,  $K$ .

### ► Practice Exercise

For the reaction



in which direction will the equilibrium shift when (a)  $\text{Cl}_2(g)$  is removed, (b) the temperature is decreased, (c) the volume of the reaction system is increased, (d)  $\text{PCl}_3(g)$  is added?

## A CLOSER LOOK Temperature Changes and Le Châtelier's Principle

By thinking of heat as a chemical reagent, we can use Le Châtelier's principle to predict how an equilibrium mixture of reactants and products will respond to a change in temperature. For an endothermic reaction, the equilibrium constant  $K$  increases as the temperature rises and decreases as the temperature is lowered, while exothermic reactions respond in the opposite manner. The underlying reason for this behavior can be understood by taking a closer look at the relationships among the equilibrium constant, the forward and reverse reaction rates, and their activation energies.

To illustrate the underlying relationships consider an elementary reaction  $A \rightleftharpoons B$ . At equilibrium, the rates of the forward and reverse reactions are equal:

$$k_f[A] = k_r[B] \quad [15.26]$$

The equilibrium constant,  $K = [B]/[A]$  can be expressed in terms of reaction rates by rearranging Equation 15.26

$$K = \frac{[B]}{[A]} = \frac{k_f}{k_r} \quad [15.27]$$

It's instructive to consider shifts in equilibrium through the lens of Equation 15.27. If the reaction in question is an endothermic reaction, a decrease in temperature will lead to a decrease in  $K$ , thereby shifting the equilibrium to the left. Equation 15.27 tells us that in order for  $K$  to decrease, the rate constant of the forward reaction  $k_f$  must decrease by a larger amount than the rate constant of the reverse reaction  $k_r$ .

To understand why  $k_f$  decreases faster than  $k_r$  consider the relationship between reaction rate and activation energy,  $E_a$ . For the sake of illustration, consider the effect of decreasing the temperature from

$T_1 = 400\text{ K}$  to  $T_2 = 300\text{ K}$ . We can calculate the change in the forward rate constant using Equation 14.23:

$$\ln \frac{k_{f1}}{k_{f2}} = \frac{E_a(\text{forward})}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad [15.28]$$

$$\ln \frac{k_{f1}}{k_{f2}} = \frac{E_a(\text{forward})}{R} \left( \frac{1}{300\text{ K}} - \frac{1}{400\text{ K}} \right) = 1200 \frac{E_a(\text{forward})}{R} \quad [15.29]$$

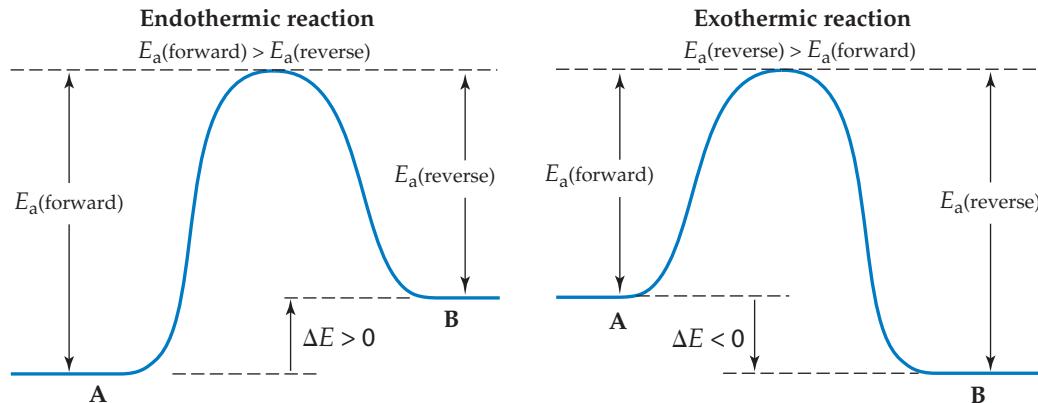
Using the same approach, we can write an equation that gives the change in the reverse rate constant:

$$\ln \frac{k_{r1}}{k_{r2}} = \frac{E_a(\text{reverse})}{R} \left( \frac{1}{300\text{ K}} - \frac{1}{400\text{ K}} \right) = 1200 \frac{E_a(\text{reverse})}{R} \quad [15.30]$$

These equations are identical with one exception: the activation energies for the forward and reverse reactions are not the same, as shown on the left-hand side of Figure 15.14. For an endothermic reaction, the activation energy in the forward direction is always larger than that of the reverse reaction,  $E_a(\text{forward}) > E_a(\text{reverse})$ . Consequently, the decrease in the forward rate constant (Equation 15.29) will be larger than the decrease in the reverse rate constant (Equation 15.30), and the overall value of the equilibrium constant  $K$  must decrease.

For an exothermic reaction,  $E_a(\text{reverse}) > E_a(\text{forward})$  and the opposite relationships apply as shown on the right-hand side of Figure 15.14. As temperature is lowered, the reverse rate constant will decrease more rapidly than the forward rate constant and the equilibrium constant  $K$  will increase; that is, the equilibrium will shift to the right.

**Related Exercises: 15.32, 15.80, 15.99, 15.104**



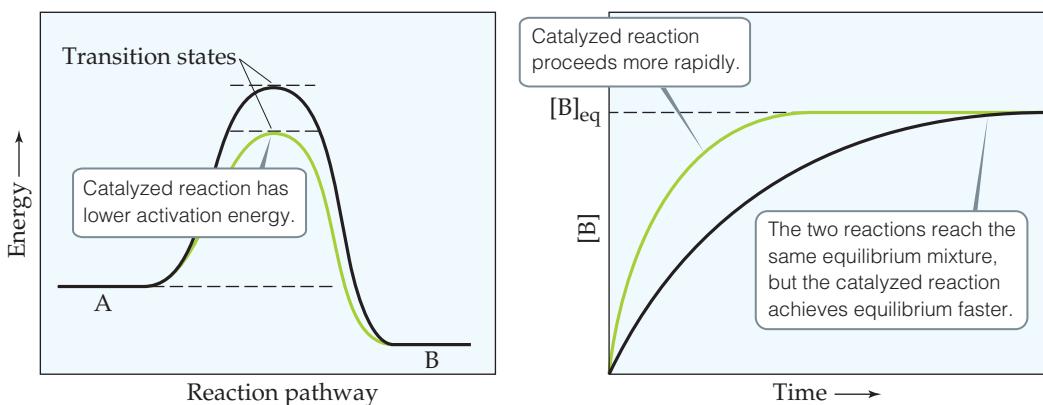
▲ Figure 15.14 The energy profile for an endothermic reaction (left) and an exothermic reaction (right).

## The Effect of Catalysts

What happens if we add a catalyst to a chemical system that is at equilibrium? As shown in Figure 15.15, 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 15.15). As a result, *a catalyst increases the rate at which equilibrium is achieved but does not change the composition of the equilibrium mixture*.

**Go Figure**

What quantity dictates the speed of a reaction: (a) the energy difference between the initial state and the transition state or (b) the energy difference between the initial state and the final state?



▲ Figure 15.15 An energy profile for the reaction  $A \rightleftharpoons B$  (left), and the change in concentration of B as a function of time (right), with and without a catalyst. Green curves show the reaction with a catalyst; black curves show the reaction without a catalyst.

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

Temperature (°C)	$K_p$
300	$4.23 \times 10^{-7}$
400	$1.60 \times 10^{-8}$
450	$4.39 \times 10^{-9}$
500	$1.41 \times 10^{-9}$
550	$5.24 \times 10^{-10}$
600	$2.19 \times 10^{-10}$

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, as you can see from Table 15.2. At temperatures sufficiently high to 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 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 20 to 60 MPa. The high pressures are needed to obtain a satisfactory equilibrium amount of  $NH_3$ . If a catalyst could be found 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 20 to 60 MPa. This would result in great savings in both the cost of the high-pressure equipment and the energy consumed in the production of ammonia. It is estimated that the Haber process consumes approximately 1% of the energy generated in the world each year. Not surprisingly, chemists and chemical engineers are actively searching for improved catalysts for the Haber process. A breakthrough in this field would not only increase the supply of ammonia for fertilizers, it would also reduce the global consumption of fossil fuels in a significant way.

## Self-Assessment Exercises

**15.25** 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?

- (a) Shift to the left
- (b) Shift to the left
- (b) No change

**15.26** Based on Le Châtelier's principle, would you predict the vapor pressure of a gas will increase or decrease as the temperature increases?

(a) Increase

(b) Decrease

**15.27** If a reaction is carried out in the presence of a catalyst, will the amount of product present at equilibrium increase, decrease, or stay the same?

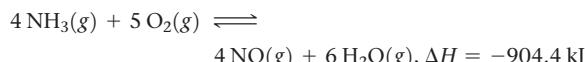
(a) Increase

(b) Decrease

(c) No change

## Exercises

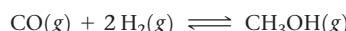
- 15.28** Consider the reaction



Does each of the following increase, decrease, or leave unchanged the yield of NO at equilibrium? (a) increase  $[\text{NH}_3]$ ; (b) increase  $[\text{H}_2\text{O}]$ ; (c) decrease  $[\text{O}_2]$ ; (d) decrease the volume of the container in which the reaction occurs; (e) add a catalyst; (f) increase temperature.

- 15.29** 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?

- 15.30** Methanol ( $\text{CH}_3\text{OH}$ ) can be made by the reaction of CO with  $\text{H}_2$ :



(a) Use thermochemical data in Appendix C to calculate  $\Delta H^\circ$  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?

- 15.31** Bromine and hydrogen react in the gas phase to form hydrogen bromide:  $\text{H}_2(g) + \text{Br}_2(g) \rightleftharpoons 2\text{HBr}(g)$ . The reaction enthalpy is  $\Delta H^\circ = -6 \text{ kJ}$ . (a) To increase the equilibrium yield of hydrogen bromide would you use high or low temperature? (b) Could you increase the equilibrium yield of hydrogen bromide by controlling the pressure of this reaction? If so, would high or low pressure favor formation of  $\text{HBr}(g)$ ?

- 15.32** (a) Is the dissociation of fluorine molecules into atomic fluorine,  $\text{F}_2(g) \rightleftharpoons 2 \text{F}(g)$  an exothermic or endothermic process? (b) If the temperature is raised by 100 K, does the equilibrium constant for this reaction increase or decrease? (c) If the temperature is raised by 100 K, does the forward rate constant  $k_f$  increase by a larger or smaller amount than the reverse rate constant  $k_r$ ?

15.25 (a) 15.26 (a) 15.27 (c)

Answers to Self-Assessment Exercises



### Sample Integrative Exercise

#### Putting Concepts Together

At temperatures near  $800^\circ\text{C}$ , steam passed over hot coke (a form of carbon obtained from coal) reacts to form CO and  $\text{H}_2$ :



The mixture of gases that results is an important industrial fuel called *water gas*. (a) At  $800^\circ\text{C}$  the equilibrium constant for this reaction is  $K_p = 14.3$ . What are the equilibrium partial pressures of  $\text{H}_2\text{O}$ , CO, and  $\text{H}_2$  in the equilibrium mixture at this temperature if we start with solid carbon and 0.100 mol of  $\text{H}_2\text{O}$  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  $25^\circ\text{C}$  the value of  $K_p$  for this reaction is  $1.7 \times 10^{-23}$ . Is the reaction exothermic or endothermic? (e) To produce the maximum amount of CO and  $\text{H}_2$  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 water.

$$P_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}RT}{V} = \frac{(0.100 \text{ mol})(8.314 \text{ L kPa/mol K})(1073 \text{ K})}{1.00 \text{ L}} = 8.92 \text{ bar}$$

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

$\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g)$				
Initial partial pressure (bar)		8.92	0	0
Change in partial pressure (bar)		$-x$	$+x$	$+x$
Equilibrium partial pressure (bar)		$8.92 - x$	$x$	$x$

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

$$K_p = \frac{P_{\text{CO}}P_{\text{H}_2}}{P_{\text{H}_2\text{O}}} = \frac{(x)(x)}{(8.92 - x)} = 14.3$$

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

$$x^2 = (14.3)(892 - x)$$

Solving this equation for  $x$  using the quadratic formula yields  $x = 6.22 \text{ bar}$ . Hence, the equilibrium partial pressures are  $P_{\text{CO}} = x = 6.22 \text{ bar}$ ,  $P_{\text{H}_2} = x = 6.22 \text{ bar}$ , and  $P_{\text{H}_2\text{O}} = (892 - x) = 2.70 \text{ bar}$ .

$$x^2 + 14.3x - 127.55 = 0$$

Continued

- (b) Part (a) shows that  $x = 6.22$  bar of  $\text{H}_2\text{O}$  must react for the system to achieve equilibrium. We can use the ideal-gas equation to convert this partial pressure into a mole amount.

Thus,  $0.0697$  mol of  $\text{H}_2\text{O}$  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.

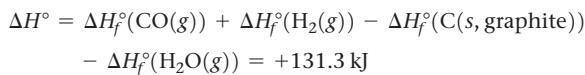
- (c) The total pressure in the vessel at equilibrium is simply the sum of the equilibrium partial pressures:

$$n = \frac{PV}{RT} \\ = \frac{(6.22 \text{ bar})(1.00 \text{ L})}{(0.08314 \text{ L bar/mol K})(1073 \text{ K})} = 0.0697 \text{ mol}$$

$$P_{\text{total}} = P_{\text{H}_2\text{O}} + P_{\text{CO}} + P_{\text{H}_2} \\ = 2.70 \text{ bar} + 6.22 \text{ bar} + 6.22 \text{ bar} = 15.14 \text{ bar}$$

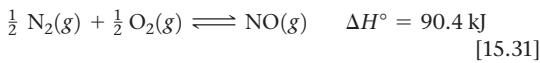
- (d) In discussing Le Châtelier's principle, we saw that endothermic reactions exhibit an increase in  $K_p$  with increasing temperature. Because the equilibrium constant for this reaction increases as temperature increases, the reaction must be endothermic. From the enthalpies of formation given in Appendix C, we can verify our prediction by calculating the enthalpy change for the reaction: The positive sign for  $\Delta H^\circ$  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 2 mol 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  $\text{H}_2$ .



## CHEMISTRY PUT TO WORK Controlling Nitric Oxide Emissions

The formation of NO from  $\text{N}_2$  and  $\text{O}_2$ ,



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  $1 \times 10^{-15}$  (Figure 15.16). At 2400 K, however, the equilibrium constant is about 0.05, which is  $10^{13}$  times larger than the 300 K value.

Figure 15.16 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 15.26 shifts to the left (because the reactant heat is being removed). However, the lower temperature also means that the reaction rate decreases, so the NO formed at 2400 K is essentially "trapped" in that form as the gas cools.

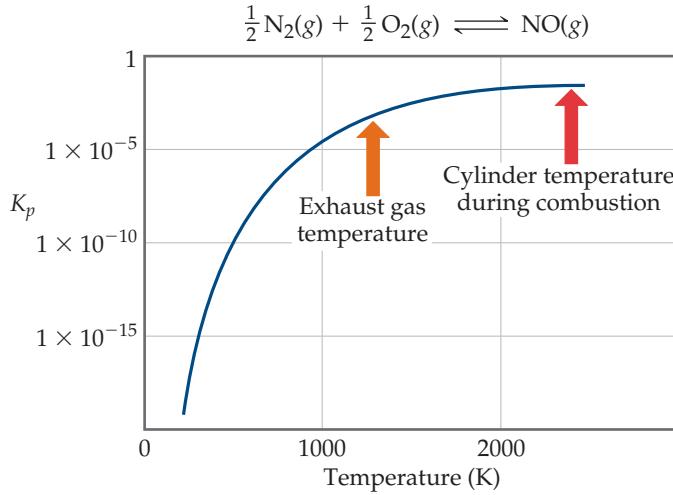
The gases exhausting from the cylinder are still quite hot, perhaps 1200 K. At this temperature, as shown in Figure 15.16, the equilibrium constant for formation of NO is about  $5 \times 10^{-4}$ , much smaller than the value at 2400 K. However, the rate of conversion of NO to  $\text{N}_2$  and  $\text{O}_2$  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  $\text{N}_2$  and  $\text{O}_2$  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 15.16 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

**THE CONCEPT OF EQUILIBRIUM (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 reactants and products. The composition of an equilibrium mixture does not change with time if temperature is held constant.

**THE EQUILIBRIUM CONSTANT (SECTION 15.2)** An equilibrium that is used throughout this chapter is the reaction  $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$ . 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  $a \text{A} + b \text{B} \rightleftharpoons d \text{D} + e \text{E}$ , the **equilibrium expression** is written as

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

where  $K_c$  is a dimensionless 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:

$$K_p = \frac{(P_{\text{D}})^d (P_{\text{E}})^e}{(P_{\text{A}})^a (P_{\text{B}})^b}$$

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

**UNDERSTANDING AND WORKING WITH EQUILIBRIUM CONSTANTS (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 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.

Equilibria can be divided into two types: **homogeneous equilibria** where all of the reactants and products are in the same phase, and **heterogeneous equilibria** where more than one phase is present.

Because their activities are exactly 1, the concentrations of pure solids and liquids are left out of the equilibrium expression for a heterogeneous equilibrium.

**CALCULATING EQUILIBRIUM CONSTANTS (SECTION 15.4)** If the concentrations of all species in an equilibrium are known, the equilibrium 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.

The **reaction quotient**,  $Q$ , is found by substituting reactant and product concentrations or partial pressures at any point during a reaction into the equilibrium 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 move toward equilibrium by forming more reactants (the reaction proceeds 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.

**LE CHÂTELIER'S PRINCIPLE (SECTION 15.5)** Le Châtelier's principle states that if a system at equilibrium is disturbed, the equilibrium will shift to minimize the disturbing influence. Therefore, 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. While changes in concentration or pressure lead to shifts in the equilibrium concentrations, they do not change the value of the equilibrium constant,  $K$ .

Changes in temperature affect both the equilibrium concentrations and the equilibrium constant. We can use the enthalpy change for a reaction to determine 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  $K$ .

## Learning Outcomes After studying this chapter, you should be able to:

- Explain what is meant by chemical equilibrium and how it relates to reaction rates. (Section 15.1)  
*Related Exercises: 15.2, 15.33, 15.45*
- Write the equilibrium expression for any reaction. (Section 15.2) *Related Exercises: 15.5, 15.46*
- Convert  $K_c$  to  $K_p$  and vice versa. (Section 15.2)  
*Related Exercises: 15.8, 15.49*
- Relate the magnitude of an equilibrium constant to the relative amounts of reactants and products present in an equilibrium mixture. (Section 15.3) *Related Exercises: 15.6, 15.47, 15.48*
- Manipulate the equilibrium constant to reflect changes in the chemical equation. (Section 15.3)  
*Related Exercises: 15.14, 15.50–15.52*
- Write the equilibrium expression for a heterogeneous reaction. (Section 15.4) *Related Exercises: 15.15, 15.39, 15.53*
- Calculate an equilibrium constant from concentration measurements. (Section 15.5)  
*Related Exercises: 15.17, 15.54–15.56*
- Predict the direction of a reaction given the equilibrium constant and the concentrations of reactants and products. (Section 15.6)  
*Related Exercises: 15.20, 15.21, 15.61, 15.62*
- Calculate equilibrium concentrations given the equilibrium constant and all but one equilibrium concentration. (Section 15.6)  
*Related Exercises: 15.22, 15.65–15.67*
- Calculate equilibrium concentrations, given the equilibrium constant and the starting concentrations. (Section 15.6)  
*Related Exercises: 15.23, 15.68, 15.72, 15.74*
- Use Le Châtelier's principle to predict how changing the concentrations, volume, or temperature of a system at equilibrium affects the equilibrium position. (Section 15.7)  
*Related Exercises: 15.28, 15.31, 15.76, 15.78*

## Key Equations

$$\bullet \quad K_c = \frac{[D]^d [E]^e}{[A]^a [B]^b} \quad [15.8]$$

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

$$\bullet \quad K_p = K_c (RT)^{\Delta n} \quad [15.15]$$

$$\bullet \quad Q_c = \frac{[D]^d [E]^e}{[A]^a [B]^b} \quad [15.24]$$

The equilibrium expression for a general reaction of the type  $a A + b B \rightleftharpoons d D + e E$ , the concentrations are equilibrium concentrations only

The equilibrium expression in terms of equilibrium partial pressures

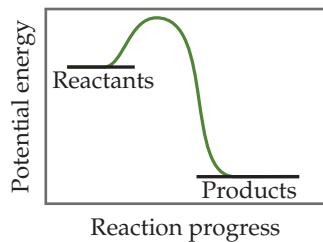
Relating the equilibrium constant based on pressures to the equilibrium constant based on concentrations

The reaction quotient. The concentrations are for any time during a reaction. If the concentrations are equilibrium concentrations, then  $Q_c = K_c$ .

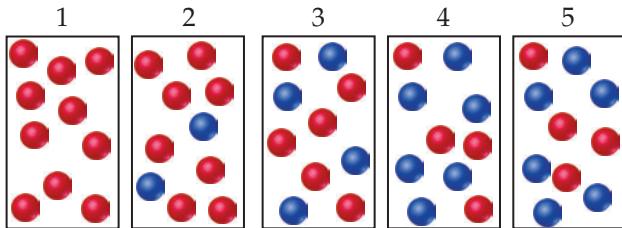
## Exercises

### Visualizing Concepts

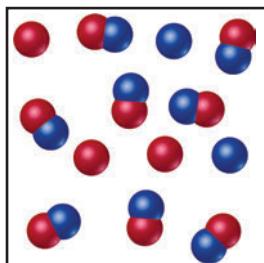
- 15.33** (a) Based on the following energy profile, predict whether  $k_f > k_r$  or  $k_f < k_r$ . (b) Using Equation 15.5, predict whether the equilibrium constant for the process is greater than 1 or less than 1. [Section 15.1]



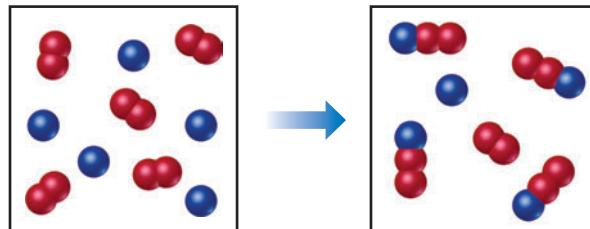
- 15.34** The following diagrams represent a hypothetical reaction  $A \rightarrow B$ , with A represented by red spheres and B represented by blue spheres. The sequence from left to right represents the system as time passes. Does the system reach equilibrium? If so, in which diagram(s) is the system in equilibrium? [Sections 15.1 and 15.2]



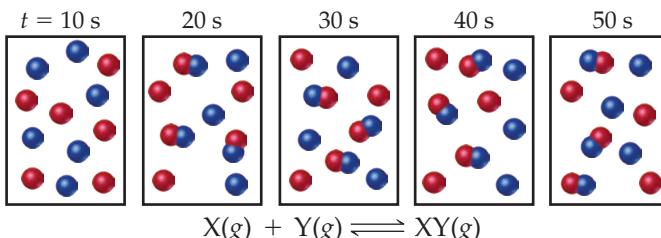
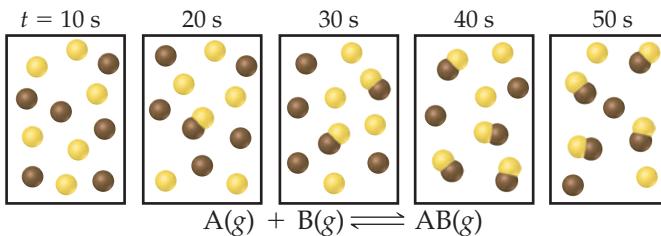
- 15.35** The following diagram represents an equilibrium mixture produced for a reaction of the type  $A + X \rightleftharpoons AX$ . Is  $K$  greater or smaller than 1 if the volume is 1 L and each atom/molecule in the diagram represents 1 mol? [Section 15.2]



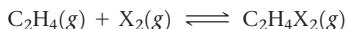
- 15.36** The following diagram represents a reaction shown going to completion. Each molecule in the diagram represents 0.1 mol, and the volume of the box is 1.0 L. (a) Letting A = red spheres and B = blue spheres, write a balanced equation for the reaction. (b) Write the equilibrium-constant expression for the reaction. (c) Calculate the value of  $K_c$ . (d) Assuming that all of the molecules are in the gas phase, calculate  $\Delta n$ , the change in the number of gas molecules that accompanies the reaction. (e) Calculate the value of  $K_p$ . [Section 15.2]



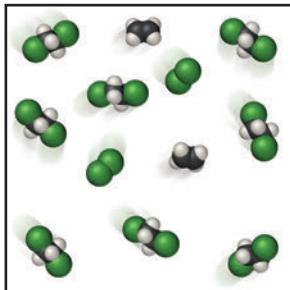
- 15.37** Snapshots of two hypothetical reactions,  $A(g) + B(g) \rightleftharpoons AB(g)$  and  $X(g) + Y(g) \rightleftharpoons XY(g)$  at five different times are shown here. Which reaction has a larger equilibrium constant? [Sections 15.1 and 15.2]



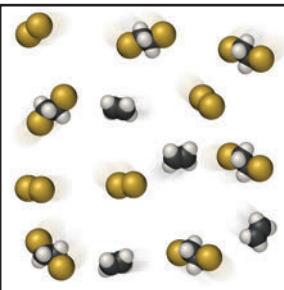
- 15.38** Ethene ( $C_2H_4$ ) reacts with halogens ( $X_2$ ) by the following reaction:



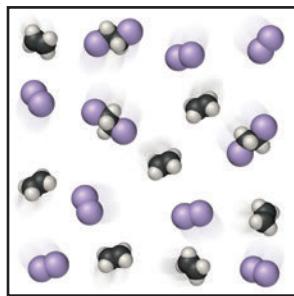
The following figures represent the concentrations at equilibrium at the same temperature when  $X_2$  is  $Cl_2$  (green),  $Br_2$  (brown), and  $I_2$  (purple). List the equilibria from smallest to largest equilibrium constant. [Section 15.3]



(a)

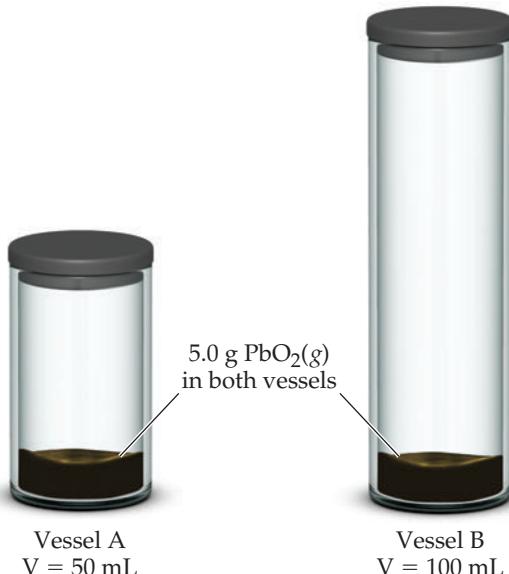


(b)

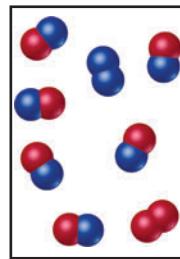


(c)

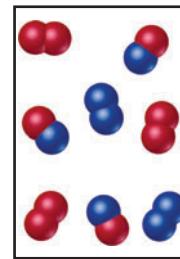
- 15.39** When lead(IV) oxide is heated above  $300^\circ\text{C}$ , it decomposes according to the following reaction  $PbO_2(s) \rightleftharpoons PbO(s) + O_2(g)$ . Consider the two sealed vessels of  $PbO_2$  shown here. If both vessels are heated to  $400^\circ\text{C}$  and allowed to come to equilibrium, which of the following statements is true? (a) There will be less  $PbO_2$  remaining in vessel A, (b) There will be less  $PbO_2$  remaining in vessel B, (c) The amount of  $PbO_2$  remaining in each vessel will be the same. [Section 15.3]



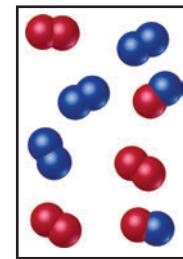
- 15.40** The reaction  $A_2 + B_2 \rightleftharpoons 2AB$  has an equilibrium constant  $K_c = 1.5$ . The following diagrams represent reaction mixtures containing  $A_2$  molecules (red),  $B_2$  molecules (blue), and  $AB$  molecules. (a) Which reaction mixture is at equilibrium? (b) For those mixtures that are not at equilibrium, how will the reaction proceed to reach equilibrium? [Sections 15.4]



(i)

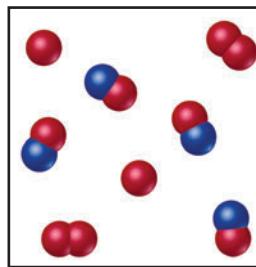


(ii)

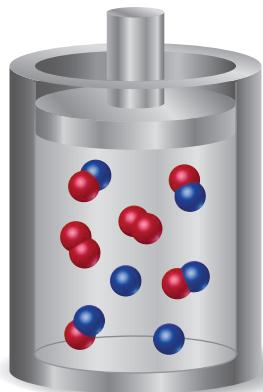


(iii)

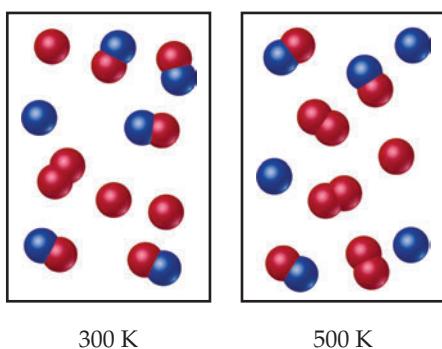
- 15.41** The reaction  $A_2(g) + B(g) \rightleftharpoons A(g) + AB(g)$  has an equilibrium constant of  $K_p = 2$ . The accompanying diagram shows a mixture containing  $A$  atoms (red),  $A_2$  molecules, and  $AB$  molecules (red and blue). How many  $B$  atoms should be added to the diagram to illustrate an equilibrium mixture? [Section 15.4]



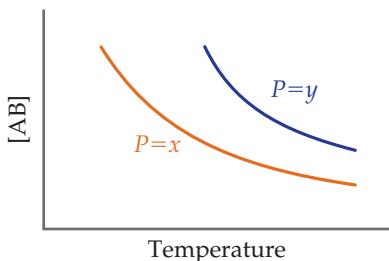
- 15.42** The diagram shown here represents the equilibrium state for the reaction  $A_2(g) + 2B(g) \rightleftharpoons 2AB(g)$ . (a) Assuming the volume is 2 L, calculate the equilibrium constant  $K_c$  for the reaction. (b) If the volume of the equilibrium mixture is decreased, will the number of  $AB$  molecules increase or decrease? [Sections 15.4 and 15.5]



- 15.43** The following diagrams represent equilibrium mixtures for the reaction  $A_2 + B \rightleftharpoons A + AB$  at 300 K and 500 K. The  $A$  atoms are red, and the  $B$  atoms are blue. Is the reaction exothermic or endothermic? [Section 15.5]



- 15.44** The following graph represents the yield of the compound AB at equilibrium in the reaction  $A(g) + B(g) \rightleftharpoons AB(g)$  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 15.5]

## Equilibrium; The Equilibrium Constant (Sections 15.1–15.3)

- 15.45** Assume that the equilibrium constant for the dissociation of molecular bromine,  $\text{Br}_2(g) \rightleftharpoons 2\text{Br}(g)$ , at 800 K is  $K_c = 5.4 \times 10^{-3}$ . (a) Which species predominates at equilibrium,  $\text{Br}_2$  or  $\text{Br}$ , assuming that the concentration of  $\text{Br}_2$  is larger than  $5.4 \times 10^{-3} \text{ mol/L}$ . (b) Assuming both forward and reverse reactions are elementary processes, which reaction has the larger numeric value of the rate constant, the forward or the reverse reaction?

- 15.46** Write the expression for  $K_c$  for the following reactions. In each case indicate whether the reaction is homogeneous or heterogeneous.

- (a)  $\text{I}_2(g) \rightleftharpoons 2\text{I}(g)$
- (b)  $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$
- (c)  $\text{CO}_2(g) + \text{C}(s) \rightleftharpoons 2\text{CO}(g)$
- (d)  $\text{H}_2\text{O}(g) + \text{CO}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$
- (e)  $\text{CO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3(aq) + \text{H}^+(aq)$
- (f)  $\text{Fe}^{2+}(aq) + \text{Zn}(s) \rightleftharpoons \text{Zn}^{2+}(aq) + \text{Fe}(s)$
- (g)  $\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)$

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

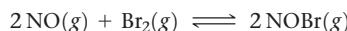
- (a)  $\text{H}_2\text{O}(g) + \text{CO}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$   
at 900 K  $K_c = 2.24$
- (b)  $2\text{CO}(g) \rightleftharpoons \text{CO}_2(g) + \text{C}(s)$   
at 1300 K  $K_p = 5.27 \times 10^{-5}$

- 15.48** Which of the following statements are true and which are false? (a) The equilibrium constant can never be a negative number. (b) In reactions that we draw with a single-headed arrow, the equilibrium constant has a value that is very close to zero. (c) As the value of the

equilibrium constant increases, the speed at which a reaction reaches equilibrium increases.

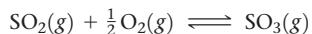
- 15.49** If  $K_c = 0.013 \text{ L/mol}$  for  $2\text{NO}(g) + \text{Br}_2(g) \rightleftharpoons 2\text{NOBr}(g)$  at 1000 K, what is the value of  $K_p$  for this reaction at this temperature?

- 15.50** The equilibrium constant for the reaction



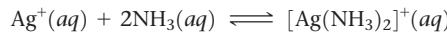
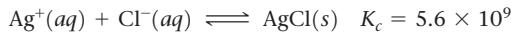
is  $K_c = 1.3 \times 10^{-2}$  at 1000 K. (a) At this temperature does the equilibrium favor NO and  $\text{Br}_2$ , or does it favor  $\text{NOBr}$ ? (b) Calculate  $K_c$  for  $2\text{NOBr}(g) \rightleftharpoons 2\text{NO}(g) + \text{Br}_2(g)$ . (c) Calculate  $K_c$  for  $\text{NOBr}(g) \rightleftharpoons \text{NO}(g) + \frac{1}{2}\text{Br}_2(g)$ .

- 15.51** At 1000 K,  $K_p = 0.184$  for the reaction



- (a) What is the value of  $K_p$  for the reaction  $\text{SO}_3(g) \rightleftharpoons \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g)$ ? (b) What is the value of  $K_p$  for the reaction  $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$ ? (c) What is the value of  $K_c$  for the reaction in part (b)?

- 15.52** The following equilibria were attained at 298 K:



$$K_c = 1.6 \times 10^7$$

Based on these equilibria, calculate the equilibrium constant for  $\text{AgCl}(s) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2(aq) + \text{Cl}^-(aq)$  at 298 K.

- 15.53** Mercury(I) oxide decomposes into elemental mercury and elemental oxygen:  $2\text{Hg}_2\text{O}(s) \rightleftharpoons 4\text{Hg}(l) + \text{O}_2(g)$ .

- (a) Write the equilibrium 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.

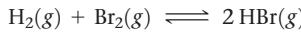
## Calculating Equilibrium Constants (Section 15.4)

- 15.54** Gaseous hydrogen iodide is placed in a closed container at 450 °C, where it partially decomposes to hydrogen and iodine:  $2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$ . At equilibrium it is found that  $[\text{HI}] = 4.50 \times 10^{-3} \text{ M}$ ,  $[\text{H}_2] = 5.75 \times 10^{-4} \text{ M}$ , and  $[\text{I}_2] = 5.75 \times 10^{-4} \text{ M}$ . What is the value of  $K_c$  at this temperature?

- 15.55** The equilibrium  $2\text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2\text{NOCl}(g)$  is established at 550 K. An equilibrium mixture of the three gases has partial pressures of 10.13 kPa, 20.27 kPa, and 35.46 kPa for NO, Cl<sub>2</sub>, 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.

- 15.56** Phosphorus trichloride gas and chlorine gas react to form phosphorus pentachloride gas:  $\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)$ . A 7.5 L gas vessel is charged with a mixture of  $\text{PCl}_3(g)$  and  $\text{Cl}_2(g)$ , which is allowed to equilibrate at 450 K. At equilibrium the partial pressures of the three gases are  $P_{\text{PCl}_3} = 12.56 \text{ kPa}$ ,  $P_{\text{Cl}_2} = 15.91 \text{ kPa}$ , and  $P_{\text{PCl}_5} = 131.7 \text{ kPa}$ . (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.

- 15.57** A mixture of 1.374 g of H<sub>2</sub> and 70.31 g of Br<sub>2</sub> is heated in a 2.00 L vessel at 700 K. These substances react according to



At equilibrium, the vessel is found to contain 0.566 g of H<sub>2</sub>. (a) Calculate the equilibrium concentrations of H<sub>2</sub>, Br<sub>2</sub>, and HBr. (b) Calculate  $K_c$ .

- 15.58** A mixture of 0.886 mol of CO<sub>2</sub>, 0.443 mol of H<sub>2</sub>, and 0.713 mol of H<sub>2</sub>O is placed in a 10.00 L vessel. The following equilibrium is established at 550 K:



- (a) Calculate the initial partial pressures of CO<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O. (b) At equilibrium  $P_{\text{H}_2} = 182 \text{ kPa}$ , calculate the equilibrium partial pressures of CO<sub>2</sub>, CO, and H<sub>2</sub>O. (c) Calculate  $K_p$  for the reaction. (d) Calculate  $K_c$  for the reaction.

- 15.59** A flask is charged with 152.0 kPa of N<sub>2</sub>O<sub>4</sub>(g) and 101.3 kPa NO<sub>2</sub>(g) at 25 °C, and the following equilibrium is achieved:



After equilibrium is reached, the partial pressure of NO<sub>2</sub> is 51.9 kPa. (a) What is the equilibrium partial pressure of N<sub>2</sub>O<sub>4</sub>? (b) Calculate the value of  $K_p$  for the reaction. (c) Calculate  $K_c$  for the reaction.

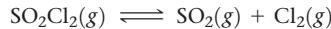
- 15.60** Two different proteins X and Y are dissolved in aqueous solution at 37 °C. The proteins bind in a 1:1 ratio to form XY. A solution that is initially 1.00 mM in each protein is allowed to reach equilibrium. At equilibrium, 0.20 mM of free X and 0.20 mM of free Y remain. What is  $K_c$  for the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

- 15.61** (a) What is the value of  $Q_c$  at the end of a certain reaction, when only products are present? (b) How will the value of  $Q_c$  change as a forward reaction proceeds? (b) What condition must be satisfied so that  $Q_c = K_c$ ?

- 15.62** At 100 °C, the equilibrium constant for the reaction  $\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$  has the value  $K_c = 2.19 \times 10^{-10}$ . Are the following mixtures of COCl<sub>2</sub>, CO, and Cl<sub>2</sub> at 100 °C at equilibrium? If not, indicate the direction that the reaction must proceed to achieve equilibrium.

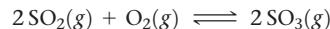
- (a)  $[\text{COCl}_2] = [\text{CO}] = 1.00 \times 10^{-4} \text{ M}$ ,  $[\text{Cl}_2] = 7.2 \times 10^{-6} \text{ M}$   
 (b)  $[\text{COCl}_2] = 2.20 \times 10^{-2} \text{ M}$ ,  $[\text{CO}] = 2.2 \times 10^{-7} \text{ M}$ ,  
 $[\text{Cl}_2] = 3.0 \times 10^{-6} \text{ M}$   
 (c)  $[\text{COCl}_2] = 0.0100 \text{ M}$ ,  $[\text{CO}] = [\text{Cl}_2] = 7.2 \times 10^{-6} \text{ M}$

- 15.63** At 120 °C,  $K_c = 0.090$  for the reaction



In an equilibrium mixture of the three gases, the concentrations of SO<sub>2</sub>, Cl<sub>2</sub>, and SO<sub>2</sub> are 0.100 M and 0.075 M, respectively. What is the partial pressure of Cl<sub>2</sub> in the equilibrium mixture?

- 15.64** At 850 K, the following reaction has  $K_p = 0.0035$ :



In an equilibrium mixture the partial pressures of SO<sub>2</sub> and O<sub>2</sub> are 18.24 kPa and 50.66 kPa, respectively. What is the equilibrium partial pressure of SO<sub>3</sub> in the mixture?

- 15.65** At 1285 °C, the equilibrium constant for the reaction Br<sub>2</sub>(g)  $\rightleftharpoons$  2 Br(g) is  $K_c = 1.04 \times 10^{-3}$ . A 1.00 L vessel containing an equilibrium mixture of the gases has 1.50 g Br<sub>2</sub>(g) in it. What is the mass of Br(g) in the vessel?

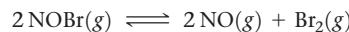
- 15.66** For the reaction, at H<sub>2</sub>(g) + I<sub>2</sub>(g)  $\rightleftharpoons$  2 HI(g),  $K_c = 55.3$  at 700 K. In a 10.0 L flask containing an equilibrium mixture of the three gases, there are 1.30 g H<sub>2</sub> and 21.0 g I<sub>2</sub>. What is the mass of HI in the flask?

- 15.67** At 800 K, the equilibrium constant for I<sub>2</sub>(g)  $\rightleftharpoons$  2 I(g) is  $K_c = 3.1 \times 10^{-5}$ . If an equilibrium mixture in a 5.00 L vessel contains 30.5 mg of I(g), how many grams of I<sub>2</sub> are in the mixture?

- 15.68** At 2000 °C, the equilibrium constant for the reaction 2 NO(g)  $\rightleftharpoons$  N<sub>2</sub>(g) + O<sub>2</sub>(g) is  $K_c = 2.4 \times 10^3$ . If the

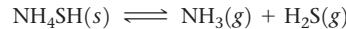
initial concentration of NO is 0.250 M, what are the equilibrium concentrations of NO, N<sub>2</sub>, and O<sub>2</sub>?

- 15.69** At 900 °C,  $K_p = 51.2$  for the equilibrium



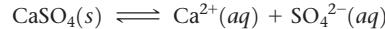
If the pressure of NO(g) is half the pressure of NOBr(g), what is the equilibrium pressure of Br<sub>2</sub>(g)?

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



Calculate the equilibrium concentrations of NH<sub>3</sub> and H<sub>2</sub>S if a sample of solid NH<sub>4</sub>SH is placed in a closed vessel at 218 °C and decomposes until equilibrium is reached.

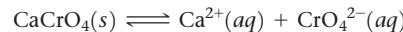
- 15.71** Consider the reaction



At 25 °C, the equilibrium constant is  $K_c = 2.4 \times 10^{-5}$  for this reaction. (a) If excess CaSO<sub>4</sub>(s) is mixed with water at 25 °C to produce a saturated solution of CaSO<sub>4</sub>, what are the equilibrium concentrations of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>? (b) If the resulting solution has a volume of 1.4 L, what is the minimum mass of CaSO<sub>4</sub>(s) needed to achieve equilibrium?

- 15.72** For the reaction I<sub>2</sub>(g) + Br<sub>2</sub>(g)  $\rightleftharpoons$  2 IBr(g),  $K_c = 310$  at 140 °C. Suppose that 1.00 mol IBr in a 5.00 L flask is allowed to reach equilibrium at 140 °C. What are the equilibrium concentrations of IBr, I<sub>2</sub>, and Br<sub>2</sub>?

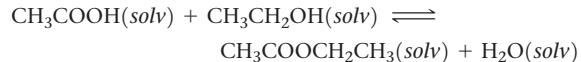
- 15.73** At 25 °C, the reaction



has an equilibrium constant  $K_c = 7.1 \times 10^{-4}$ . What are the equilibrium concentrations of Ca<sup>2+</sup> and CrO<sub>4</sub><sup>2-</sup> in a saturated solution of CaCrO<sub>4</sub>?

- 15.74** Methane, CH<sub>4</sub>, reacts with I<sub>2</sub> according to the reaction CH<sub>4</sub>(g) + I<sub>2</sub>(g)  $\rightleftharpoons$  CH<sub>3</sub>I(g) + HI(g). At 600 K,  $K_p$  for this reaction is  $1.95 \times 10^{-4}$ . A reaction was set up at 600 K with initial partial pressures of methane of 13.3 kPa and of 6.67 kPa for I<sub>2</sub>. Calculate the pressures, in kPa, of all reactants and products at equilibrium.

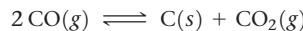
- 15.75** The reaction of an organic acid with an alcohol, in organic solvent, to produce an ester and water is commonly done in the pharmaceutical industry. This reaction is catalyzed by strong acid (usually H<sub>2</sub>SO<sub>4</sub>). A simple example is the reaction of acetic acid with ethyl alcohol to produce ethyl acetate and water:



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 15.5)

- 15.76** Consider the following exothermic equilibrium (Boudouard reaction)



How will each of the following changes affect an equilibrium mixture of the three gases: (a) a catalyst is added to the mixture; (b) CO<sub>2</sub>(g) is added to the system; (c) CO(g) is added from the system; (d) the reaction mixture is heated; (e) the volume of the reaction vessel is doubled; (f) the total pressure of the system is increased by adding a noble gas?

- 15.77** How do the following changes affect the value of the  $K_p$  for a gas-phase endothermic reaction: (a) increase in the total pressure by adding a noble gas, (b) addition of a reactant, (c) increase in the temperature (d) increase in the volume, (e) decrease in the temperature?

- 15.78** Consider the following equilibrium between oxides of nitrogen



- (a) Use data in Appendix C to calculate  $\Delta H^\circ$  for this reaction.  
 (b) Will the equilibrium constant for the reaction increase or

decrease with increasing temperature? (c) At constant temperature, would a change in the volume of the container affect the fraction of products in the equilibrium mixture?

- 15.79** Ozone,  $\text{O}_3$ , decomposes to molecular oxygen in the stratosphere according to the reaction  $2 \text{O}_3(g) \longrightarrow 3 \text{O}_2(g)$ . Would an increase in pressure favor the formation of ozone or of oxygen?

- 15.80** True or false: When the temperature of an exothermic reaction increases, the rate constant of the forward reaction decreases, which leads to a decrease in the equilibrium constant,  $K_c$ .

## Additional Exercises

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

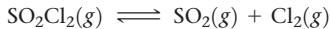


At 25 °C, the rate constants for the forward and reverse reactions are  $1.4 \times 10^{-28} \text{ M}^{-1} \text{ s}^{-1}$  and  $9.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , respectively. (a) What is the value for the equilibrium constant at 25 °C? (b) Are reactants or products more plentiful at equilibrium?

- 15.82** If  $K_c = 1$  for the equilibrium  $3\text{A}(g) \rightleftharpoons 2\text{B}(g)$ , what is the relationship between [A] and [B] at equilibrium?

- 15.83** A mixture of  $\text{CH}_4$  and  $\text{H}_2\text{O}$  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  $\text{H}_2$ , 43.0 g of  $\text{CH}_4$ , and 48.4 g of  $\text{H}_2\text{O}$ . Assuming that equilibrium has been reached, calculate  $K_c$  and  $K_p$  for the reaction  $\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3 \text{H}_2(g)$ .

- 15.84** When 2.00 mol of  $\text{SO}_2\text{Cl}_2$  is placed in a 5.00 L flask at 310 K, 40% of the  $\text{SO}_2\text{Cl}_2$  decomposes to  $\text{SO}_2$  and  $\text{Cl}_2$ :



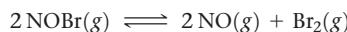
(a) Calculate  $K_c$  for this reaction at this temperature.  
 (b) Calculate  $K_p$  for this reaction at 310 K. (c) According to Le Châtelier's principle, would the percent of  $\text{SO}_2\text{Cl}_2$  that decomposes increase, decrease or stay the same if the mixture was transferred to a 1.00 L vessel? (d) Use the equilibrium constant you calculated to determine the percentage of  $\text{SO}_2\text{Cl}_2$  that decomposes when 2.00 mol of  $\text{SO}_2\text{Cl}_2$  is placed in a 1.00 L vessel at 310 K.

- 15.85** The value of the equilibrium constant  $K_c$  for the reaction  $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$  changes in the following manner as a function of temperature

Temperature (°C)	$K_c$
300	9.6
400	0.50
500	0.058

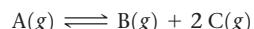
(a) Based on the changes in  $K_c$  is this reaction exothermic or endothermic? (b) Use the standard enthalpies of formation given in Appendix C to determine the  $\Delta H^\circ$  for this reaction at standard conditions. Does this value agree with your prediction from part (a)? (c) If 0.025 mole of gaseous  $\text{NH}_3$  is added to a 1.00 L container and heated to 500 °C, what is the concentration of  $\text{NH}_3$  once the sample reaches equilibrium?

- 15.86** A sample of nitrosyl bromide ( $\text{NOBr}$ ) decomposes according to the equation



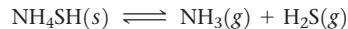
An equilibrium mixture in a 5.00 L vessel at 100 °C contains 3.22 g of  $\text{NOBr}$ , 3.08 g of NO, and 4.19 g of  $\text{Br}_2$ . (a) Calculate  $K_c$ . (b) What is the total pressure exerted by the mixture of gases? (c) What was the mass of the original sample of  $\text{NOBr}$ ?

- 15.87** Consider the hypothetical reaction



A flask is charged with 100 kPa of pure A, after which it is allowed to reach equilibrium at 25 °C. At equilibrium, the partial pressure of B is 25 kPa. (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?

- 15.88** Solid  $\text{NH}_4\text{SH}$  is introduced into an evacuated flask at 24 °C. The following reaction takes place:



At equilibrium, the total pressure (for  $\text{NH}_3$  and  $\text{H}_2\text{S}$  taken together) is 0.62 bar. What is  $K_p$  for this equilibrium at 24 °C?

- 15.89** At 900 °C,  $K_c = 0.0108$  for the reaction



A mixture of  $\text{CaCO}_3$ ,  $\text{CaO}$ , and  $\text{CO}_2$  is placed in a 10.0 L vessel at 900 °C. For the following mixtures, will the amount of  $\text{CaCO}_3$  increase, decrease, or remain the same as the system approaches equilibrium?

- (a) 15.0 g  $\text{CaCO}_3$ , 15.0 g  $\text{CaO}$ , and 4.25 g  $\text{CO}_2$   
 (b) 2.50 g  $\text{CaCO}_3$ , 25.0 g  $\text{CaO}$ , and 5.66 g  $\text{CO}_2$   
 (c) 30.5 g  $\text{CaCO}_3$ , 25.5 g  $\text{CaO}$ , and 6.48 g  $\text{CO}_2$

- 15.90** When 1.50 mol  $\text{CO}_2$  and 1.50 mol  $\text{H}_2$  are placed in a 3.00 L container at 395 °C, the following reaction occurs:  $\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)$ . If  $K_c = 0.802$ , what are the concentrations of each substance in the equilibrium mixture?

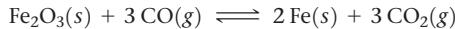
- 15.91** The equilibrium constant  $K_c$  for  $\text{C}(s) + \text{CO}_2(g) \rightleftharpoons 2 \text{CO}(g)$  is 1.9 at 1000 K and 0.133 at 298 K. (a) If excess C is allowed to react with 25.0 g of  $\text{CO}_2$  in a 3.00 L vessel at 1000 K, how many grams of CO are produced? (b) How many grams 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?

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



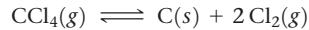
At 1600 K, the equilibrium constant for the reaction is  $K_p = 6.0 \times 10^2$ . If a CO pressure of 0.20 bar is to be employed in the furnace and total pressure never exceeds 1.0 bar, will reduction occur?

- 15.93** 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  $\text{CO}_2$  according to the reaction



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 30 m. 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?

- 15.94** At 700 K, the equilibrium constant for the reaction



is  $K_p = 77$ . A flask is charged with 202.7 kPa of  $\text{CCl}_4$ , which then reaches equilibrium at 700 K. **(a)** What fraction of the  $\text{CCl}_4$  is converted into C and  $\text{Cl}_2$ ? **(b)** What are the partial pressures of  $\text{CCl}_4$  and  $\text{Cl}_2$  at equilibrium?

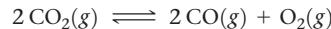
- 15.95** The reaction  $\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)$  has  $K_p = 8.59 \times 10^{-4}$  at 300 °C. A flask is charged with 50.7 kPa  $\text{PCl}_3$ , 50.7 kPa  $\text{Cl}_2$ , and 20.3 kPa  $\text{PCl}_5$  at this temperature. **(a)** Use the reaction quotient 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  $\text{Cl}_2$  in the equilibrium mixture? **(d)** The reaction is exothermic. What effect will increasing the

temperature of the system have on the mole fraction of  $\text{Cl}_2$  in the equilibrium mixture?

- 15.96** An equilibrium mixture of  $\text{H}_2$ ,  $\text{I}_2$  at HI at 500 °C contains 0.150 mol  $\text{H}_2$ , 0.150 mol  $\text{I}_2$  and 1.000 mol HI in a 10.00 L vessel. What are the equilibrium partial pressures when equilibrium is reestablished following the addition of 0.100 mol of HI?

- 15.97** Consider the hypothetical reaction  $\text{A}(g) + 2 \text{B}(g) \rightleftharpoons 2 \text{C}(g)$ , 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.)

- 15.98** At 1200 K, the approximate temperature of automobile exhaust gases (Figure 15.14),  $K_p$  for the reaction



is about  $1 \times 10^{-11}$ . Assuming that the exhaust gas (total pressure 1 atm) contains 0.2% CO, 12%  $\text{CO}_2$ , and 3%  $\text{O}_2$  by volume, is the system at equilibrium with respect to the  $\text{CO}_2$  reaction? Based on your conclusion, would the CO concentration in the exhaust be decreased or increased by a catalyst that speeds up the  $\text{CO}_2$  reaction? Recall that at a fixed pressure and temperature, volume% = mol%.

- 15.99** At a temperature of 700 K, the forward and reverse rate constants for the reaction  $2 \text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g)$  are  $k_f = 1.8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  and  $k_r = 0.063 \text{ M}^{-1} \text{ s}^{-1}$ . **(a)** What is the value of the equilibrium constant  $K_c$  at 700 K? **(b)** Is the forward reaction endothermic or exothermic if the rate constants for the same reaction have values of  $k_f = 0.097 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_r = 2.6 \text{ M}^{-1} \text{ s}^{-1}$  at 800 K?

## Integrative Exercises

- 15.100** Consider the reaction  $\text{IO}_4^-(aq) + 2 \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_4\text{IO}_6^-(aq)$ ;  $K_c = 3.5 \times 10^{-2}$ . If you start with 25.0 mL of a 0.905 M solution of  $\text{NaIO}_4$ , and then dilute it with water to 500.0 mL, what is the concentration of  $\text{H}_4\text{IO}_6^-$  at equilibrium?

- 15.101** The following equilibria were measured at 823 K:

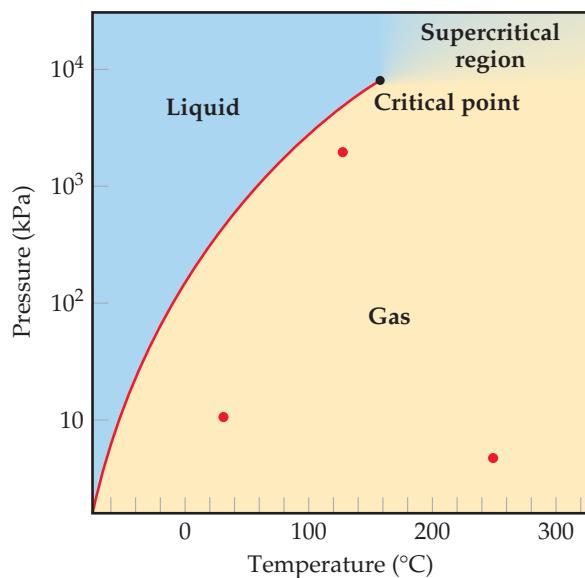


**(a)** Use these equilibria to calculate the equilibrium constant,  $K_c$ , for the reaction  $\text{CoO}(s) + \text{CO}(g) \rightleftharpoons \text{Co}(s) + \text{CO}_2(g)$  at 823 K. **(b)** Based on your answer to part (a), would you say that carbon monoxide is a stronger or weaker reducing agent than  $\text{H}_2$  at  $T = 823$  K? **(c)** If you were to place 5.00 g of  $\text{CoO}(s)$  in a sealed tube with

a volume of 250 mL that contains  $\text{CO}(g)$  at a pressure of 1 atm and a temperature of 298 K, what is the concentration of the CO gas? Assume there is no reaction at this temperature and that the CO behaves as an ideal gas (you can neglect the volume of the solid). **(d)** If the reaction vessel from part (c) is heated to 823 K and allowed to come to equilibrium, how much  $\text{CoO}(s)$  remains?

- 15.102** Consider the equilibrium  $\text{A} \rightleftharpoons \text{B}$  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.

- 15.103** The phase diagram for  $\text{SO}_2$  is shown here. (a) What does this diagram tell you about the enthalpy change in the reaction  $\text{SO}_2(l) \rightarrow \text{SO}_2(g)$ ? (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  $\text{SO}_2(g)$  most closely approach ideal gas behavior? (e) At which of the three red points does  $\text{SO}_2(g)$  behave least ideally?



- 15.104** At 800 K, the equilibrium constant for the reaction  $\text{A}_2(g) \rightleftharpoons 2\text{A}(g)$  is  $K_c = 3.1 \times 10^{-4}$ . (a) Assuming both forward and reverse reactions are elementary reactions, which rate constant do you expect to be larger,  $k_f$  or  $k_r$ ?

- (b) If the value of  $k_f = 0.27 \text{ s}^{-1}$ , what is the value of  $k_r$  at 800 K? (c) Based on the nature of the reaction, do you expect the forward reaction to be endothermic or exothermic? (d) If the temperature is raised to 1000 K, will the reverse rate constant  $k_r$  increase or decrease? Will the change in  $k_r$  be larger or smaller than the change in  $k_f$ ?

- 15.105** 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?

- 15.106** Water molecules in the atmosphere can form hydrogen-bonded dimers,  $(\text{H}_2\text{O})_2$ . 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?

- 15.107** The protein hemoglobin (Hb) transports  $\text{O}_2$  in mammalian blood. Each Hb can bind 4  $\text{O}_2$  molecules. The equilibrium constant for the  $\text{O}_2$  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 2.53 kPa, and adult hemoglobin has a P50 value of 3.57 kPa. Use these data to estimate how much larger  $K_c$  is for the aqueous reaction  $4\text{O}_2(g) + \text{Hb}(aq) \rightleftharpoons [\text{Hb}(\text{O}_2)_4(aq)]$  in a fetus, compared to  $K_c$  for the same reaction in an adult.

## Design an Experiment

The reaction between hydrogen and iodine to form hydrogen iodide was used to illustrate Beer's law in Chapter 14 (Figure 14.5). The reaction can be monitored using visible-light spectroscopy because  $\text{I}_2$  has a violet color while  $\text{H}_2$  and  $\text{HI}$  are colorless. At 300 K, the equilibrium constant for the reaction  $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$  is  $K_c = 794$ . To answer the following questions assume you have access to hydrogen, iodine, hydrogen iodide, a transparent reaction vessel, a visible-light spectrometer, and a means for changing the temperature.

- (a) Which gas or gases concentration could you readily monitor with the spectrometer? (b) To use Beer's law (Equation 14.5), you need to determine the extinction coefficient,  $\epsilon$ , for the substance in question. How would you determine  $\epsilon$ ? (c) Describe an experiment for determining the equilibrium constant at 600 K. (d) Use the bond enthalpies in Table 8.3 to estimate the enthalpy of this reaction. (e) Based on your answer to part (d), would you expect  $K_c$  at 600 K to be larger or smaller than at 300 K?